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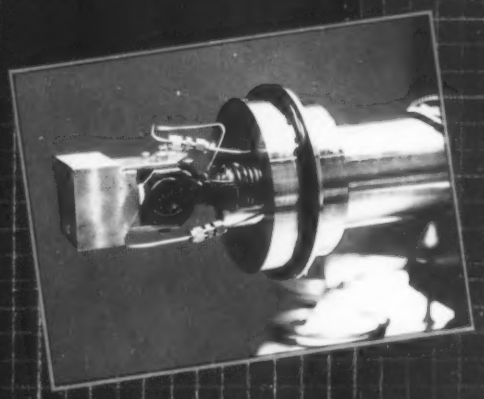

Diamond Anvil Cell

Left to right,
Wilbur Perry and Professor John Strong examining
the first double-screw ruling engine.

Professor Strong developed this engine with funding from the Office of Naval Research at The Johns Hopkins University about 1950 and brought new dimensions to the art of diffraction gratings. Wilbur Perry was the machinist who maintained the engine and produced some of the best gratings of the time.

Diffraction gratings are reflection surfaces on which about 15,000 groves are ruled per inch. These groves are capable of diffracting light in such a way that many interferring beams produce spectra. The production, measurement, and interpretation of electromagnetic spectra, arising either from emission or absorption of radiant energy by various substances, is the science of spectroscopy.

The double-screw ruling engine made it possible to have better control over the shape and size of diffracting groves and made gratings which were freer from mechanical error, wasted less light, and gave higher resolving power. Such advances benefited astronomical spectroscopy, atomic spectroscopy, and radio astronomy.

John Strong is today Professor Emeritus of Physics and Astronomy at the University of Massachusetts at Amherst. He recognized his collegue Wilbur Perry as a mechanical genious. "If the double-screw ruling engine were a Stradivarous violin, Wilbur Perry was the superb musician or technician who could play it the best." Perry drew the majority of gratings on which the interpretation of atomic spectra are based. Professor Strong's double-screw ruling engine is the ancestor of the five in use throughout the world today.

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ABOUT THE COVER

Photograph of the world's first high pressure – low temperature installation at a synchrotron radiation source, viz., a Be-Cu diamond-anvil pressure cell coupled to the low temperature end of a closed cycle cryogenic helium refrigerator. The equipment was first used at the Stanford Synchrotron Radiaton Laboratory, Stanford University in January, 1983. See article beginning on page 20.

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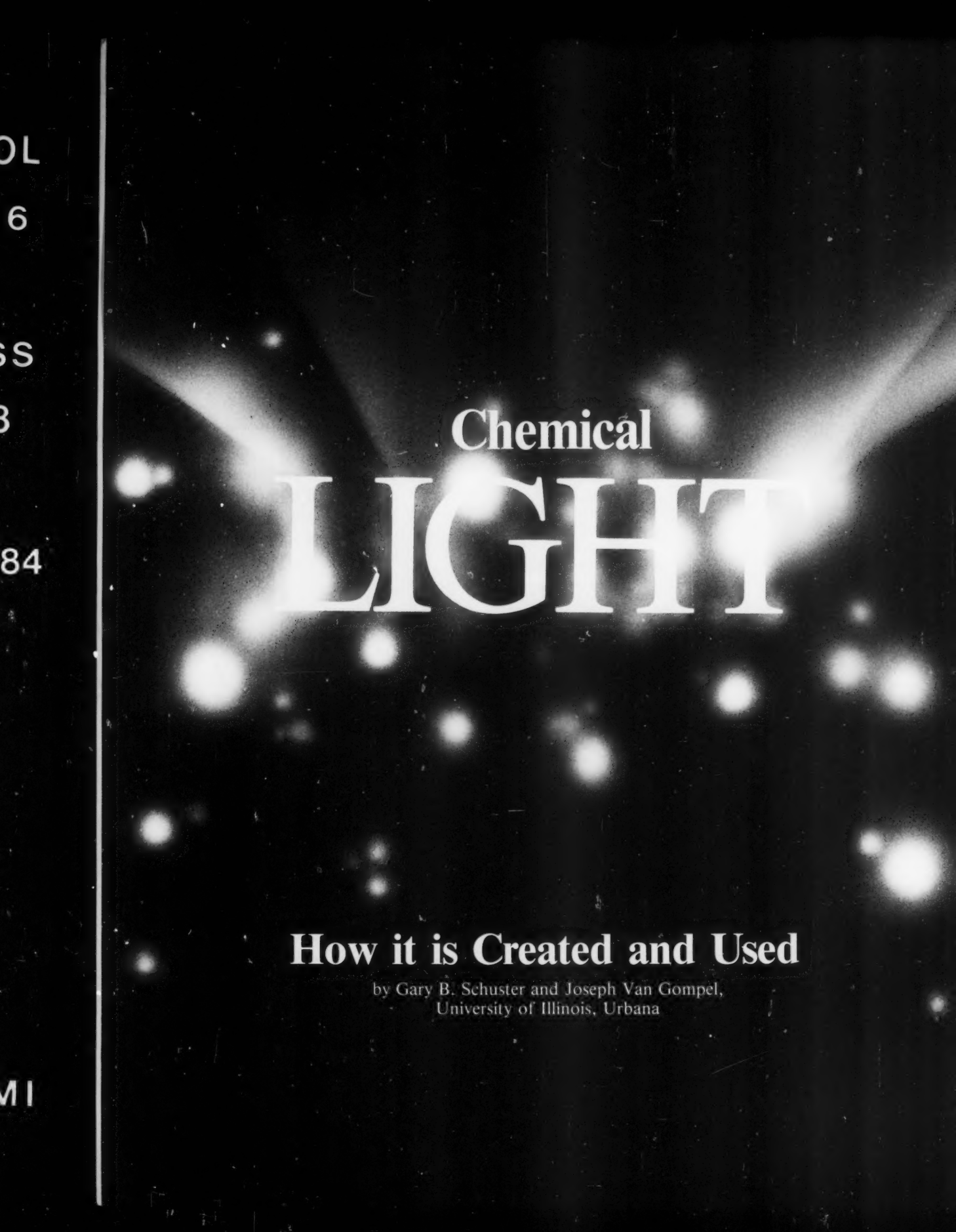

Chemical
LIGHT
How it is Created and Used
by Gary B. Schuster and Joseph Van Gompel,
University of Illinois, Urbana

It is abundantly clear that discoveries giving man ability to generate and control visible light have played central roles in the development of our culture and technology. In a comparatively brief period of time, we have moved from candles to lasers and replaced ignorance and fear with specific knowledge and understanding of the chemical and physical basis for light generation. It is fair to say that the investigation of light is inexorably linked with nearly all of our greatest scientific and technological achievements. Our language makes it unequivocal; to "see" something is to finally understand it.

In this article, we attempt to trace and explain the development of a small part of the pursuit of control over light. Chemiluminescence and bioluminescence are two phenomena related by the fact that for both a chemical reaction leads to light. Both are familiar, and yet they retain an aura of mystery. The goal of our research and of this article is to replace that mystery with understanding. Our hope is that this understanding will lead to new uses for this unusual way of generating and controlling light.

The generation of light is an electronic phenomenon. The ground state of a molecule has its electronic energy at the lowest possible value. At normal temperatures the electrons are found in pairs in the low energy occupied orbitals so that their number just balances the positive nuclear charge. Energy can be added to molecules. The additional energy may change the distribution of electrons in orbitals. Movement of an electron from one of the relatively low energy occupied orbitals to a higher energy previously unoccupied orbital creates an excited state.

Electronically excited states of molecules are metastable entities. Typically, they exist only for a very small fraction of a second before giving up their excess energy and returning to the ground state. The excess energy can be released in several forms. It may become internal, vibrational energy of the molecule by a process called internal conversion, or it may be emitted as light. Thus, on a microscopic scale, light generation is a consequence of the radiative deactivation of an electronically excited state. Non-radiative deactivation (internal conversion) is a far more common event. Thus, light generation is limited to a few favorable reactions.

The way energy is added to create the electronically excited state differentiates various forms of light generation. Two broad categories are incandescence and luminescence. The former, generally, is a consequence of heating. When the temperature of a material is raised, energy flows into it and is distributed among the various mechanical and electronic modes. The number and nature of the excited states formed in this way is governed in part by statistics, and the light emitted is called "black-body radiation." The intensity and wavelength (color) of black-body radiation are determined by the temperature. If incandescence can be likened to a shotgun blast, luminescence is analogous to a rifle shot. Thus, instead of adding energy randomly to a substance, concentrating it in formation of electronically excited states results in light emission in excess of the black-body level. This excess light emission is luminescence, and it is a consequence of populating excited states to levels greater than expected from the random distribution of energy at a particular temperature. In this regard, luminescence can be thought of as "cold light."

There are several ways to concentrate energy in the formation of electronically excited states. The simplest, conceptually, is photoluminescence. In this process, incident light is absorbed by a substance and an electron is promoted from an occupied to an unoccupied orbital. Soon thereafter the excited state thus formed may emit light as it returns from the excited to the ground state. In essence, this sequence can be summarized as light in - light out. However, the light out often has different properties than the light in. For example, the wavelength of the emitted light is typically longer than that of the absorbed light. A longer wavelength corresponds to a lower energy, and this energy loss is due to relaxation of the excited state after it is formed, but before it emits. One form this relaxation often takes is a change in the spin of the electrons involved. If the spin of the emitting excited state is different from that of the ground state, the photoluminescence is called phosphorescence. If the spin of these two states is the same, then the emission is called fluorescence. Relaxation before emission is often a critical requirement for materials useful as active media in lasers.

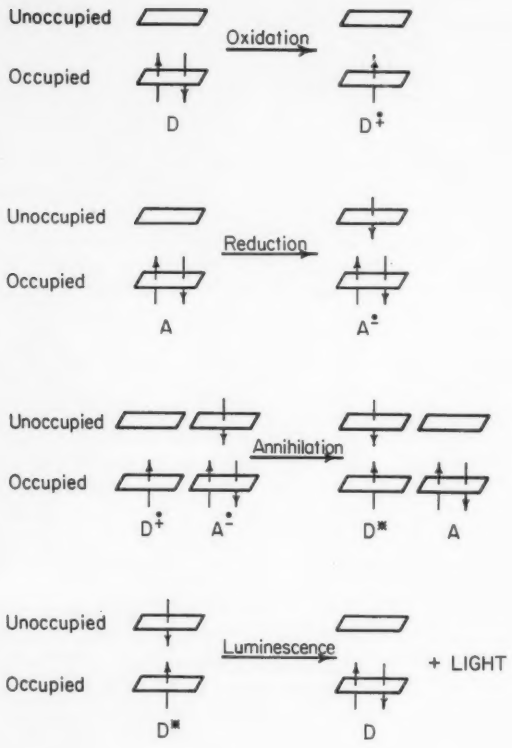
The energy required for luminescence can come from sources other than light. An electrical discharge, for example, powers the familiar neon lamp. Mechanical energy is converted to light in triboluminescence, and chemical energy is converted to light in chemiluminescence. In all of these examples, the final step is the same: radiative deactivation of an electronically excited state. A focus of research in chemiluminescence is to understand how the chemical potential energy of bonds in molecules is converted into electronically excited states. In the remainder of this article, we will present the current understanding of this energy transduction and describe some of the useful properties of this unusual way to generate light.

Chemiluminescence and Bioluminescence

The modern history of chemiluminescence starts with the discovery of luminol in 1928. However, fascination with naturally occurring chemiluminescence and bioluminescence certainly predates any surviving record. Many people are familiar with fireflies, and few will not admit to wondering how this creature can create light. Less familiar, though more common, are sea creatures that generate light. Examples range from simple one-celled photobacterium through jellyfish, worms, squid, shrimp, and fish. Though great in organistic variety, recent research has shown that light generation in living systems has

Figure 1

Electrogenerated Chemiluminescence



its basis in one or two chemical reaction mechanisms. We will develop these mechanisms first for relatively uncomplicated chemical examples and return later to their application in living systems.

Chemical Mechanisms of Chemiluminescence

The visible portion of the electromagnetic spectrum ranges from about 400 nm (violet) to 700 nm (red). The energy thus required to generate visible light corresponds to the release of 40–80 kcal/mole or 2–3.5 eV. For the purpose of comparison, many simple chemical transformations occur with the gain or loss of considerably less energy than this. Thus, only a few chemical transformations are sufficiently energy releasing (exergonic) to offer any hope for visible light generation. In this article, we will limit ourselves to processes that occur in solution, although gas-phase chemiluminescence is an active and growing area of investigation. The solution phase reactions that are sufficiently exergonic to generate visible light are limited mainly to the annihilation of oppositely charged ions, decomposition of organic peroxides, rearrangement of strained hydrocarbons, and the combination of radical fragments. These general processes form the core around which much of the understanding of chemiluminescence and bioluminescence is built.

Electrogenerated Chemiluminescence. Light generation from the annihilation of oppositely charged radical ions was first observed independently in several laboratories about twenty years ago. The precursor ions may be prepared as stable solutions and then mixed to generate light, or they may be generated *in situ* electrochemically. The latter process is called electrogenerated luminescence (ECL), and it has served as the vehicle for much of the investigation of this light-generating reaction. Incidentally, light-emitting-diodes are solid-state examples of the ECL phenomenon.

A simple diagram serves to illustrate the basic principles underpinning the formation of electronically excited states (and hence light) from ion annihilations. Recall that most neutral molecules contain two electrons in their highest occupied orbital, and that in the ground state the lowest unoccupied oribital is empty. Two ions are required for the annihilation process; the first comes from some substance we will call D (for donor) and the second from A (for acceptor). The highest occupied and lowest unoccupied orbitals of D and A are indicated as bars in Figure 1, and the electron occupancy of the orbitals is indicated with arrows whose direction represents spin. In an actual ECL system, several reactions occur simultaneously. For our analysis we will consider them one at a time.

Oxidation corresponds to the removal of electrons from a substance. The first step in the ECL sequence is the one electron oxidation of D. This is accomplished at an electrode set at a voltage (relative to a reference electrode) sufficiently positive to remove a single electron from the

highest occupied orbital of D. When typical organic molecules are used as donors, they are initially neutral and contain closed electron shells. This means that there is one electron for every proton, and for every electron with spin "up" there is one with spin "down." Removing a single electron changes the balance. There is one more proton than electron, and the species has a net positive charge (a cation). Similarly, there are now an odd number of electrons, so there must be an uncompensated spin (a radical). Thus, oxidation of D converts it into a radical cation ($D^{+\cdot}$).

Reduction corresponds to the addition of electrons to a substance. This can be accomplished by setting the voltage of an electrode sufficiently negative to inject an electron into the unoccupied orbital of the acceptor. This process also unbalances charge and spin, and reduction of A converts it into a radical anion ($A^{-\cdot}$).

In the ECL process $D^{+\cdot}$ and $A^{-\cdot}$ are created either simultaneously at two different electrodes or sequentially by stepping the voltage at a single electrode. In either case, after they are formed, these radical ions diffuse through the solution and can meet each other. Typically, on every encounter of these oppositely charged radical ions a discharge occurs. In this reaction, an electron is transferred from $A^{-\cdot}$ to $D^{+\cdot}$, and an electronically excited state can be created. It is clear how this occurs. Movement of the extra electron from $A^{-\cdot}$ to the unoccupied orbital of $D^{+\cdot}$ rebalances the charge, but leaves D with only one electron each in the highest occupied and lowest unoccupied orbitals. This is just the arrangement we identified earlier as the lowest energy excited state (D^*). Radiative deactivation of D^* gives visible light and regenerates D.

There are two final features of the ECL process we need to consider. These are energy sufficiency and total electron spin.

The energy required to form light is supplied by the electrode reactions and passes through the radical ions before it is released by the annihilation step. The energy released in this step must be at least as great as the energy required to form the lowest excited state from the ground state of the eventual emitter (ΔE^*). Fortunately, the energy balance can be calculated simply from equation 1 where E_{ox} is the oxidation potential of D, E_{red} is the reduction potential of A, and E_{coul} is a coulombic work term associated with bringing oppositely charged particles toward each other. Satisfaction of equation 1 is a necessary but not a sufficient condition

$$\Delta E^* \leq E_{ox} - E_{red} + E_{coul} \qquad (1)$$

for efficient light formation by ECL. The factors other than energy sufficiency that control the efficiency of ECL are the object of current research.

The odd-electron intermediates created in the ECL sequence break the spin parity of even electron molecules. The relative spins of the unmatched electrons $D^{+\cdot}$ and $A^{-\cdot}$ may be paired (singlet) or parallel (triplet) when the two ions meet to annihilate. Paired spins can lead to a singlet excited state. Since the ground state must be a singlet, the emission obtained in this case is fluorescence which can be relatively efficient. On the other hand, when the excited state formed is a triplet, the emission is phosphorescence and is usually much less efficient. If high light efficiency is the goal, the formation of singlet excited states must be encouraged. The factors that determine the spin distribution in ion annihilation reactions are currently under investigation. One intriguing possibility is control of this parameter with magnetic fields.

Dioxetane Chemiluminescence. A second general class of chemiluminescent reactions involves the conversion of a single reagent with high energy content directly to an electronically excited state product. Unlike ECL, which involves only electron transfer, these chemiluminescent transformations are more complex because they require breaking old bonds and making new bonds between atoms. There is an almost infinite variety of structures falling into many different classes that can undergo reactions to generate light. In many cases, the specific details of the chemical transformations are still hotly debated by active researchers. Nevertheless, in the past few years, general, but by no means unanimous, agreement about some details of these reactions has been achieved. We will present a few examples of the more thoroughly studied of these chemiluminescent reactions indicating where uncertainty of detail remains to be resolved.

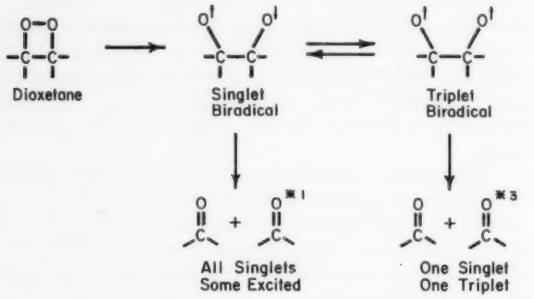
Dioxetanes are organic peroxides in which the peroxide linkage (oxygen to oxygen bond) is constrained in a four-membered ring. The peroxide bond is found nearly universally in chemi- and bioluminescent reagents. This is not an accident. Recall that between 40 and 80 kcal/mole must be available to generate a visible photon. The peroxide linkage is a relatively weak bond; and in many reactions of organic peroxides, it is converted eventually into a carbon to oxygen double linkage (carbonyl group) which is a very strong bond. The energy released in the conversion of a peroxide bond to carbonyl groups is available to form an excited state and hence generate light. This feature is present in the reactions of dioxetanes, equation 2, where cleavage of the oxygen-oxygen bond and a carbon-carbon bond forms two carbonyl compounds, i.e. tetramethyldioxetane becomes two molecules of acetone.

(2)

Dioxetanes possess a second feature that contributes to energy release. The four-membered ring distorts some bonds away from their preferred angles. This distortion is removed when the ring is broken and considerable strain energy is released. These factors combine to make a reaction of equation 2 exothermic by about 70 kcal/mole,

Figure 2

Dioxetane Decomposition



sufficient to generate visible light. However, energy sufficiency is not the only prerequisite to excited state formation. Indeed, there are energy-sufficient systems that are not chemiluminescent. Obviously, some mechanism must be available to channel the bond and strain energy toward excited states. Nevertheless, several researchers were moved to suggest a pivotal role for dioxetanes in chemi- and bioluminescence long before they were actually prepared and isolated. Subsequent investigations have shown that some of these suggestions are in fact correct.

The first dioxetane to be characterized was prepared by Canadian scientists in 1969. They observed that trimethyldioxetane is stable, and that when it is heated in solution it fragments to give acetone, acetaldehyde and blue light. Since the initial report, literally hundreds of different dioxetanes have been prepared in various research laboratories around the world. The chemical and physical properties of these substances have been scrutinized by nearly every conceivable technique to try and unravel the mechanism of light generation. It is not within the scope of this article to review the data supporting the current view of this mechanism. Instead, we will summarize the present position and indicate where most of the remaining uncertainty lies.

There are two rather distinct classes of dioxetanes. This fact was not recognized until quite recently, and attempts to understand the properties of all dioxetanes within one framework led to considerable confusion. The two classes are distinguished by the nature of the substituents on the carbons of the four-membered ring. Simple alkyl (fully saturated carbon) substituents give dioxetanes that have good stability and give mainly triplet excited states when they fragment. On the other hand, dioxetanes with substituents with easily released electrons (amino groups, NH_2) are much less stable and give a much higher yield of singlet excited states when they react. We will discuss the second class further below in connection with chemically initiated electron-exchange luminescence. Here we will concentrate on the first group.

One of the central questions concerning fragmentation of dioxetanes is whether the oxygen-oxygen and carbon-carbon bonds break simultaneously or sequentially. The first process is called concerted, and rules associated with the conservation of orbital symmetry suggest that excited states should be formed by this reaction. The sequential mode proceeds through an intermediate in which two singly occupied orbitals exist (a biradical). The spins of the electrons in these orbitals may become unpaired, and the singlet ground state of the dioxetane can become a triplet biradical. Fragmentation of the second bond of the triplet biradical without further spin change is expected to give one carbonyl compound ground state and one excited state with triplet spin. Most of the experimental evidence that has been accumulated supports the second pathway to excited state formation. This sequence is illustrated in Figure 2.

The yield of excited states from simple dioxetanes can range up to about 30 percent. This is concentrated almost entirely as triplets, and the triplet of most carbonyl compounds phosphoresce vary inefficiently in solution. Thus, though the yield of excited states from dioxetanes is high, the direct yield of light is quite low. The situation can be salvaged, however, by energy transfer.

Within the short lifetime of an excited state, it is possible for the energy to migrate from one molecule to another. Thus the initial excited state formed in a chemiluminescent reaction need not be the ultimate emitter. The triplet carbonyl excited states formed from dioxetanes can transfer energy to form relatively efficiently emitting excited states of some substituted aromatic hydrocarbons. The result is indirect chemiluminescence, and it can be hundreds of times brighter than the direct chemiluminescence obtained when the triplet carbonyl compound is the emitter. It is important to note that the added energy acceptor does not change the basic character of dioxetane chemistry. It simply provides an efficient route to convert already-formed excited states into light. These same aromatic hydrocarbon acceptors play a very different active role in the chemiluminescence of other substances.

Although much is known about dioxetane chemiluminescence, it is still not possible to predict with certainty the efficiency of excited state generation or even the location of the excitation when an unsymmetrical dioxetane reacts. Several theories have been formulated that take account of such things as the specific nature of

the orbitals involved, and the possibility of complex (exciplex) formation preceeding locally excited state generation. Current research is addressing these and other important questions.

Dioxetanes are simply the most intensively studied of a group of organic peroxides that appear to generate light by proceeding through a biradical intermediate. Other examples include ozonides, six-membered ring diperoxides, and some peroxyesters. We will not discuss these other cases beyond noting that they also appear to generate predominantly triplet excited states.

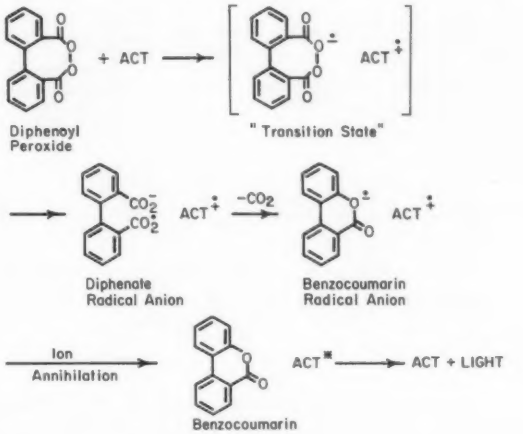
Chemically Initiated Electron-Exchange Luminescence. It was suspected for some time that peroxides play a central role in bioluminescence. However, their proclivity to triplet excited state formation seemed inconsistent with the very high yield of singlets observed in the living systems. This was resolved by the discovery that certain peroxides under special reaction conditions formed excited states by a novel mechanism that did indeed give a high yield of singlet excited states. This mechanism is called chemically initiated electron-exchange luminescence (CIEEL). It has certain features in common with both ECL and with the chemistry of dioxetanes. Recent research appears to indicate that the CIEEL process underlies all the most efficient chemi- and bioluminescent systems.

The starting point for CIEEL is typically a high-energy content organic peroxide. In contrast to simple dioxetanes, however, the initiation of the energy-releasing sequence is not bond cleavage, but is rather electron transfer from a donor molecule. These donors are typically easily oxidized, highly fluorescent materials, such as aromatic hydrocarbons or amines. As will be seen momentarily, the hydrocarbon, or amine, serves several functions in the CIEEL sequence, and since there is often no light formed without this additive, it is called the activator (ACT).

The CIEEL sequence is illustrated in Figure 3 for diphenoyl peroxide; one of the most thoroughly studied examples. Peroxides as a class, and diacyl peroxides in particular, are very easily reduced compounds. Diphenoyl peroxide is a diacyl peroxide since there are two carbonyl groups flanking the oxygen-oxygen bond linkage. The first step on the path leading to eventual light formation in this case is an electron transfer from the ACT to the peroxide to form a radical ion pair. The structure of the initial ion pair is uncertain since peroxide radical ions are unstable. Theoretical quantum chemical calculations indicate that the oxygen-oxygen bond of this ion cleaves spontaneously to give, in the case of diphenoyl peroxide, diphenate radical anion. This intermediate is also very short-lived. It looses carbon dioxide and cyclizes to become benzocoumarin radical anion. This sequence of reactions has in essence converted the peroxide radical anion, which has the odd electron at relatively low potential, to benzocoumarin radical anion, which has the odd electron at high reducing potential.

Figure 3

Chemically Initiated Electron-Exchange Luminescence (CIEEL)



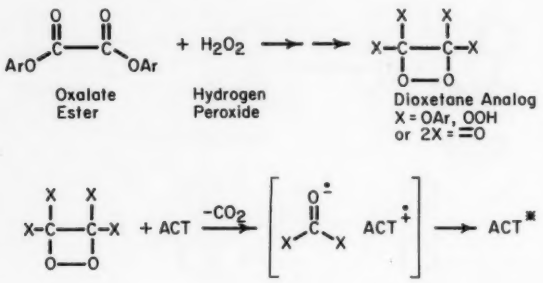
The energy required to move the electron from low to high potential is supplied by conversion of the weak oxygen-oxygen bond of the peroxide to the strong carbonyl bonds of carbon dioxide and benzocoumarin.

The evidence suggests that the transformation from peroxide and ACT to benzocoumarin radical anion and activator radical cation ($ACT^{+\cdot}$) is so fast that it is completed while the partners are nearest neighbors following the initial encounter. Thus, the radical ions from this sequence are formed within a common "solvent cage." Annihilation of oppositely charged radical ions is the penultimate step in the ECL reactions described earlier. The CIEEL sequence arrives at this same point, but from a different route. Annihilation of benzocoumarin radical anion and $ACT^{+\cdot}$ gives the activator in the excited state (ACT^*). Radiative deactivation of this state generates the observed light.

An important feature of the CIEEL sequence is that it can give a high yield of singlet excited states. Both the activator and the peroxide are singlet ground state molecules, and thus the initial radical ion pair should be a singlet. If spins do not change before the annihilation step, then the excited activator will be formed entirely in the singlet state. If the spins of the radical ions are fully equilibrated before annihilation, then a 1:3 ratio of singlet to triplet excited states is expected.

Figure 4

Oxalate Ester Chemiluminescence



In practice, both extremes appear to be operating. The most efficient examples of chemiluminescence by the CIEEL path involving separate peroxide and activator molecules form singlets with about 25 percent yield. In some bioluminescent examples, where both the activator and the peroxide are within the same molecule, the yield of singlet excited states is nearly 100 percent. We will have more to say about bioluminescence later. Next we will discuss the most efficient chemiluminescent system known, oxalate esters – the energy source of the popular light sticks.

Oxalate Ester Chemiluminescence. The discovery and development of chemiluminescence from the reaction of oxalic acid derivatives with hydrogen peroxide provides interesting lessons in serendipity and cooperation. The chemical reactions involved, although simple on the surface, shroud a degree of complexity that denies a clear look at the energy transduction. Although much is known about this system, there is still much to be learned. Here we will present in broad outline a description of what is known, and indicate the areas of the continuing investigation.

The mechanism of the chemiluminescence from oxalic acid derivatives is shown in Figure 4. The first steps in the sequence lead to the creation of an appropriate high-energy content peroxide. This is accomplished by the reaction of hydrogen peroxide with an oxalate ester prepared specially so that its carbonyl groups are susceptible to irreversible addition. The rate of formation of the appropriate peroxide can be controlled by adjusting the acidity of the solution, and this permits modification of the lifetime and the intensity of the light generation. These variables eventually effect the ultimate utilization of chemiluminescent devices based on these reactions.

The structure of the peroxide actually responsible for light generation in these reactions of oxalic acid derivatives remains unknown. Some have speculated that it is a dioxetanedione (2x= =0), and analogs of this structure are known to be chemiluminescent. Nevertheless, it seems unlikely that a strained carbonyl compound, such as the dioxetanedione, would exist for long in the presence of hydrogen peroxide. Another possibility is that several four-membered ring peroxides equilibrate in solution, and that one, or more, of these react with the activator to give the observed light. In this scenario, the dioxetanedione may be the key intermediate in the production of excited states but never builds up to an otherwise detectable concentration in solution. This sequence is consistent with the observation that the light-producing intermediate can be stable in solution in the absence of an activator.

The uncertainties remaining in the details of the structure of the key intermediate complicate the analysis of the reaction mechanism. Some facts are clear though. All other things being equal, it appears that the efficiency of light generation depends on the oxidation potential of the activator. Also, in contrast to simple dioxetanes, the oxalates give a high yield of singlet excited states. For these reasons, it has been suggested that the CIEEL reaction sequence operates here. Verification of this proposal awaits further research.

Despite the incomplete understanding of the details of the reaction mechanism, oxalate ester chemiluminescence is remarkably useful in a practical sense. We will discuss the applications of chemical light further below. Here we will point out some of the important features of the oxalate system that contribute to its utility.

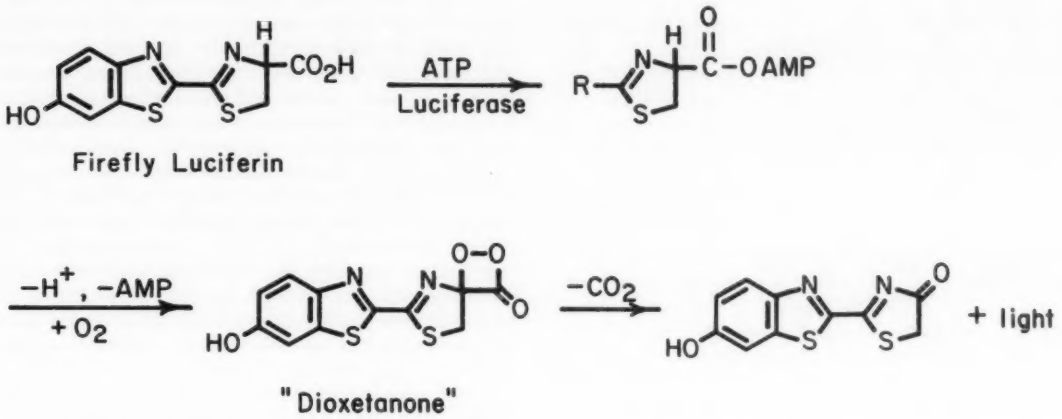
The reagents necessary to generate light from oxalate esters are stable before they are mixed. This permits initiation of the reaction at will. For example, in one device hydrogen peroxide is mixed with a solution of oxalate ester to initiate the light-generating sequence.

Control over the color of the chemiluminescent light emission can be achieved by proper choice of the activator. In all cases, the light obtained corresponds to activator fluorescence. It has proved possible to tune the wavelength of emitted light from the near ultra-violet through the visible, and into the infra-red. This flexibility is critically important in some applications.

The intensity and duration of the chemiluminescence of oxalate esters can be controlled by basic catalysts, solvent, and temperature. As the basicity of the medium is increased, the intensity of light emission goes up, and the reaction duration goes down. Thus at high pH a short-lifetime relatively bright light source is obtained. Similarly at low temperatures, the light generation slows down, and the intensity decreases; but the duration is enhanced. The opposite occurs at high temperature. Solvent choice allows some selection in, for example, the light intensity and duration at a specified temperature.

Figure 5

Firefly Bioluminescence



The Chemistry of Bioluminescence

The best-known and most studied bioluminescent organism is the North American Firefly. These insects use light to attract and identify an appropriate mate. The control mechanism, how the light is turned on and off, is still uncertain, but many of the details of the biochemical reactions leading to ultimate light generation have been uncovered.

The firefly system belongs to a class of bioluminescent reactions known as luciferin – luciferase transformations. The luciferase is an enzyme that catalyzes the oxidation and concomitant transformation to an excited state of the luciferin. The structure of firefly luciferin is well-known, and the mechanism of light formation is reasonably well understood. The details of the enzyme structure remain largely unexplored.

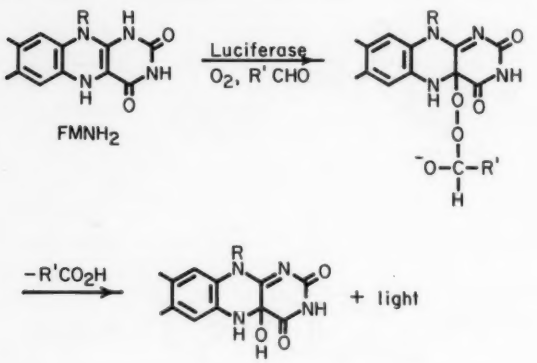
The biochemical transformations of the firefly are shown in Figure 5. The first steps involve conversion of the luciferin into a dioxetanone. This is accomplished by the enzyme using oxygen and adenosine triphosphate (ATP). This dioxetanone has never been isolated. However, other more simply substituted examples have been prepared and analyzed in great detail. They appear to generate light primarily by the pathway identified above as CIEEL. It has been suggested that an intramolecular version of the CIEEL sequence occurs in the firefly dioxetanone. Thus, both the high-energy peroxide and the activator are located within the same molecule. This juxtaposition may serve two useful purposes. First, the unstable dioxetanone is less likely to decompose spontaneously by a "dark" non-CIEEL route when the two components are linked. Second, when the odd-electrons are located in different parts of the same molecule, their spins are less likely to become unpaired; and singlet excited state formation is more probable. It is suspected that these factors contribute to the approximately 90 percent efficiency observed for firefly bioluminescence.

Some evidence supporting the importance of the intramolecularity of the firefly system comes from an analysis of specially substituted dioxetanes. We noted above that dioxetanes with electron-donating groups attached react by a different mechanism than their more simply substituted counterparts. These special dioxetanes are considerably less stable, and give a much higher yield of singlet excited states than the simply substituted variety. These findings have been taken as evidence that linking the two components of the CIEEL sequence does indeed enhance the light generating ability.

Many of the other bioluminescence organisms that have been studied appear to follow the pattern established for the firefly. A luciferin is converted enzymatically to a dioxetanone linked directly to a group capable of acting both as an electron donor and as an emitter. The details of luciferin structure vary from one species to another, but the chemical basis for light generation seems to be constant.

Figure 6

Bacterioluminescence



An exception to this generalization is bacterioluminescence. Luminous bacteria are responsible for the light generation of some sea creatures with whom they live symbiotically. For example, the light organs of some fish are infected with these bacteria.

A current version of the biochemical transformations believed to be involved in bacterioluminescence is shown in Figure 6. Reduced flavin mononucleotide ($FMNH_2$) reacts in the presence of an enzyme with oxygen and an aldehyde (R–CHO) to form a metastable intermediate. This intermediate is believed to fragment eventually to give the appropriate carboxylic acid (RCO_2H) and an excited state of the hydroxylated flavin. Light emission is thought to occur from this excited state, and the hydroxy flavin is eventually recycled to reduced flavin.

Many aspects of this proposed mechanism are well-supported by experiment. However, attempts to model the key conversion of the peroxide to an excited state with simpler analogs has so far been somewhat disappointing. Only very weak light emission has been obtained. For this reason there remains considerable uncertainty in the details of this step. However, various proposals, many centered on a version of the CIEEL sequences, are being actively investigated.

Practical Applications of Chemiluminescence and Bioluminescence

It is fair to say that the development of practical applications of chemiluminescence and bioluminescence is still in its infancy. Nevertheless, these unusual reactions have proven to be valuable in a number of areas. We will discuss two of these here: analytical applications and special lighting or marking uses. These currently are the most highly developed and often used applications of chemical light.

There are two very important features in the application of chemiluminescence to analysis. These are the very low levels of light that can be detected by sensitive photomultiplier tubes and the high degree of specificity built into most chemi- and bioluminescent reactions. Coupled, these properties permit specific detection of very low concentrations of material. Nowhere is this more important than the clinical laboratory where detection of miniscule concentrations of antibodies or hormones in biological fluids is necessary. There is currently a world-wide effort underway to incorporate these luminescent reactions into important diagnostic assays. These efforts are focused on the discovery of new reagents based on the principles discussed above and on the utilization of already known reagents in novel schemes.

Clinical Analysis Using Chemi- and Bioluminescence

As outlined in Figure 5, ATP is one of the required substrates participating in light generation from the firefly reaction. This fact has been used to develop a series of clinical assays for ATP. Information on ATP concentration in turn can be used in the analysis of, for example, electron transport linked phosphorylation or cell lysis. Alternatively, firefly luciferase can be directly bonded to antigens, and these conjugates are then used in competitive binding assays of free antigens. This technique is especially useful in immunoassays where analyte concentrations as low as 10^{-12} molar are not uncommon.

In a similar vein, bacterioluciferase has been used to detect and quantify very low levels of $FMNH_2$. This compound is identified in Figure 6 as having central importance in this light forming process. The concentration of $FMNH_2$ is typically coupled to generation or depletion of a reagent needed to produce it from the oxidized form. In this mode, the assay is remarkably versatile and has been used to detect such diverse substances as TNT (the explosive), testosterone (a male hormone), and hexokinase (an enzyme) at picomole (10^{-12}) levels.

The biological selectivity of immunoassays has been linked to the native sensitivity of chemiluminescence. In a typical "sandwich" assay, a sample containing the antigen of interest reacts with a specific antibody usually immobilized on a solid phase. Next, the antigen-antibody complex formed in the first step is exposed to a fresh antibody which has been specially labeled with a chemiluminescent reagent. Thus, the three parts of the sandwich are (1) antibody on solid phase, (2) antigen, and (3) specially labeled antibody. In principle, the next step is quite easy; simply activate the chemiluminescent reaction and measure the light output. In practice, there are several difficulties. The most critical is that most of the efficient

chemiluminescent reactions that have been developed work best in organic solvents, and the "biology," of course, works only in water. As a consequence most of the chemiluminescent immunoassays that have been developed use the less efficient light generators. Nevertheless, even with this compromise, an assay for thyroxine (a thyroid hormone) and for hepatitis antigen using luminol derivatives have been reported. It is felt by some that eventually chemiluminescence-based detection will become the most important immunoassay technique.

Special Lighting Uses. By far the most common current use of chemiluminescence is to provide lighting under conditions where conventional light generation is inconvenient or specially hazardous. The Cyalume lightsticks manufactured by the American Cyanamid Company have found widespread applicability in this regard.

The lightsticks are supplied as a plastic tube wrapped in foil to prevent light and moisture from degrading the contents. The tube is flexible and contains a solution of an oxalate ester and activator and hydrogen peroxide sealed in a glass ampule. When the plastic tube is bent, the glass ampule is shattered, and the released hydrogen peroxide initiates the reactions shown in Figure 4.

Several formulations of the lightstick are available. They vary in the identity of the fluorescer and in the concentration of added basic catalyst. This provides control of the color of the emitted light (blue, red, and green are three popular choices) and the duration of the light forming reaction. Two currently available formulations provide a two hour stick that gives very bright light and a twelve hour stick that is somewhat less intense.

The uses to which these lightsticks are put are as varied as the people who use them. They offer three major advantages over conventional light sources. First, there is no required maintenance—no batteries to run down or bulbs to burn out. Second, they are not a source of ignition—no electrical sparks, and no hot filament. Third, they work when wet, even underwater.

This last feature is very valuable in naval applications, such as underway replenishment, synthetic apeture radar, and target marking.

Other important uses of the lightsticks derive from their safety. In some circumstances, it is necessary to operate in potentially hazardous environments such as mines where the concentration of methane may be high or chemical areas where leaks of flammable or explosive agents have occurred. In these cases, the availability of chemical light may provide a margin of safety unachievable with any other device. This consideration has led National Aeronautics and Space Administration to specify lightstick use during the decontamination of the Spaceshuttle Challenger after its first night landing.

Conclusion

Chemical light generation is still in its very early stages. The scientific basis for this phenomenon is just now being clearly revealed. However, even with the limited knowledge already in hand, significant and important applications of this phenomenon in a number of areas have been made. One can now clearly see that further research into the basic mysteries of these unique processes will lead to development and fabrication of devices that may have critical military and civilian uses.

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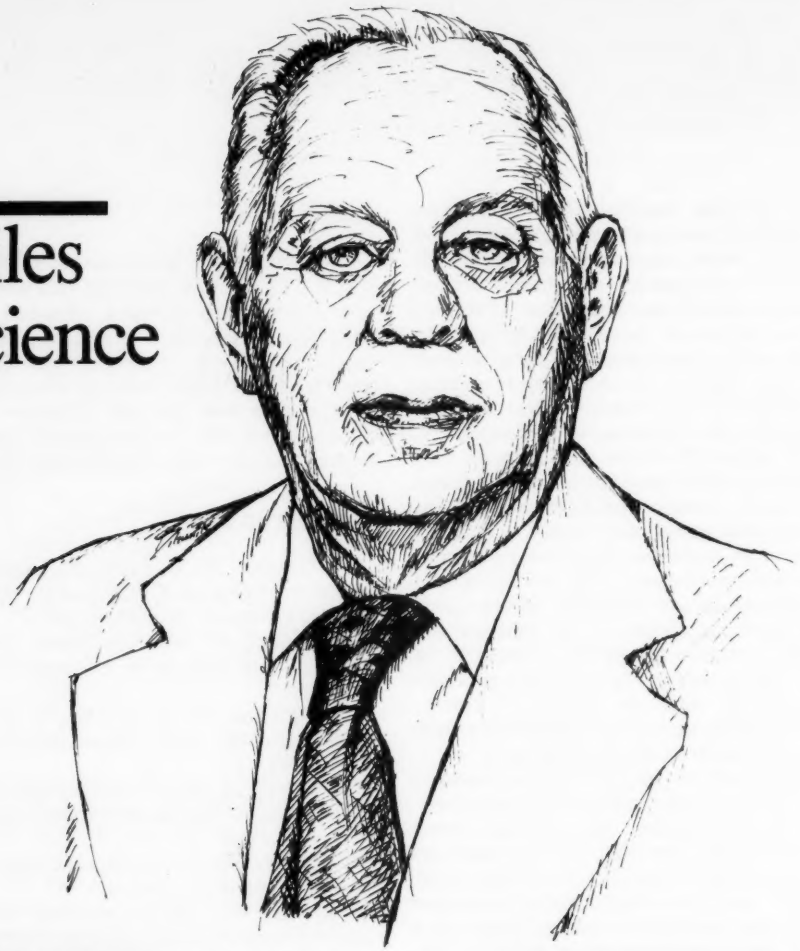
Profiles in Science



Martin Greenspan, former Chief of the Sound Section of the National Bureau of Standards (NBS), who is considered by some the "Guru of physical acoustics," has been a principal investigator and consultant to the Office of Naval Research (ONR) for 36 years. Since his retirement in 1974, he has remained a consultant at NBS and in that capacity is involved with ONR-supported research today.

Early in his career, Martin Greenspan worked in the field of elasticity and strength of materials. He performed important theoretical work on the stress distribution in civil engineering structures such as rigid knee bends, box girders, and perforated plates which are considered landmark developments to modern elastic fracture mechanics.

In physical acoustics, he pioneered research on the propagation of sound in rarefied gases which is now the classic work in the field. He was able to show that the Navier-Stokes equation gave a surprisingly good quantitative account of the attenuation and dispersion of sound in monatomic gases down at a wavelength over mean free path ratio approaching unity.

The Navy realized in the early 1950's that it needed an automatic device to measure the speed of sound in the sea, particularly as a funciton of depth. This need was remedied by Greenspan and his colleague Carl Tschiegg, who under ONR funding, developed the acoustic velocimeter. They also collaborated on cavitation research, studying the effects of dissolved gases and neutron irradiation on the threshold of cavitation. This research brought him worldwide recognition.

In 1979, Greenspan succeeded in extending the piston radiator theory to include exact solutions for cases in which the acoustic pressure and particle velocity vary over the face of the piston, which is a major contribution to the theory.

Martin Greenspan's achievements have been acknowledged with many honors. He is a Fellow of the Acoustical Society of America, the American Physical Society, the Washington Academy of Science, the American Association for the Advancement of Science, and is a member of the Philosophical Society of Washington. In addition to two Meritorious Service Awards from NBS, he received the Acoustical Society Silver Medal in Physical Acoustics in 1977, the Harry Diamond Award given by the IEEE in 1980. When he was awarded in 1983 the Gold Medal of the Acoustical Society of America, it was noted that his encyclopedic knowledge and his ability to analyze research problems have not only added new dimensions to the field of physical acoustics but have guided many scientists in the right direction.

Biological Aspects of Corrosion of Offshore Structures

by Marianne Walch and Ralph Mitchell
Harvard University

Marine corrosion is a potential hazard to all metals and alloys and to virtually every structure in contact with the sea. Corrosion of offshore structures is a major source of operational problems and economic loss. Frequently engineers fail to realize that a large proportion of marine corrosion may be initiated or assisted by the attachment and growth of bacteria and other marine organisms.[1] Since the first recognition of biological corrosion processes nearly 80 years ago, corrosion of metals by microbial activity has emerged as an important economic problem. A wide range of corrosion phenomena in which microorganisms are involved has been recognized.[2] For example, bacteria are thought to be responsible for more than 75 percent of the corrosion in productive oil wells in the United States[3] and for over half of the failures of buried pipelines and cables.[4] The economic costs of biologically-induced marine corrosion are not known, but fouling by marine micro- and macroorganisms can greatly alter the corrosion behavior of metals, as well as impair the efficient operation of marine engineering systems.

Recognition of the close relationship between biofouling and corrosion is important since prevention of biological corrosion may require a unique set of tools; knowledge of the mechanisms involved will determine the choice of alloys, coatings, etc., to be used in a particular marine environment. In this paper, we will discuss the way in which films of microorganisms form on metals placed in the ocean and some of the specific corrosion reactions which may occur either directly or indirectly as a result of the activity of these organisms. Because the corrosion of metals in contact with seawater is a major source of operational problems and economic loss to the Navy, ONR has been supporting research for many years in this field. The research described here provides for the first time a clear understanding of specific corrosion reactions that are mediated biochemically by microorganisms. The ultimate goal is to gain the ability to control biologically induced corrosion.

Biofilm Formation

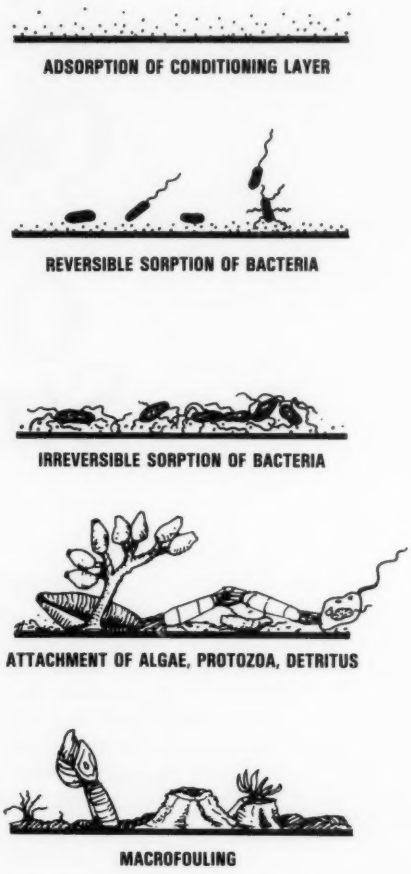
All solid surfaces, when exposed to seawater, are immediately colonized by microorganisms. Metal interfaces in aquatic systems represent sites of intense microbial activity. After immersion of only a week or two in the ocean, metal surfaces can harbor complex communities of growing bacteria, protozoa, and algae. All metals are susceptible to microfouling, even the "antifouling" copper-nickel alloys.

Our understanding of the mechanisms and significance of microbial attachment to surfaces has progressed rapidly in recent years, and the basic sequence of events in marine biofilm formation has been clarified by microbiologists[5] (see Figure 1). Immediately upon immersion of any solid in seawater, before any colonization by bacteria, a layer of organic macromolecules — called a "conditioning film" — is spontaneously adsorbed to its surface. This conditioning layer is important in establishing a base for subsequent buildup of the microfouling layer, for only after adsorption of this organic film can microorganisms attach effectively to the surface. The spontaneous adsorption of dissolved glycoproteins and other organic compounds from the aqueous phase alters the surface free energy of the solid, and these compounds may then serve as nutrients for the microorganisms that later colonize the surface.

In the next phase of the biofouling process, microorganisms arriving near the solid/liquid interface are subjected to short-range attractive forces (i.e., electrostatic, hydrophobic, and van der Waals forces) which balance the double-layer repulsive force and hold the bacteria weakly near the surface. This period is termed "reversible sorption" because the bacteria are easily removed at this stage.[6] Some bacteria which are motile may be attracted to

Figure 1

Sequence of events in biofilm formation on surfaces in seawater.



the nutrient gradient established near the interface and actively swim toward such surfaces.[7] Transport of nonmotile microorganisms to surfaces, on the other hand, depends upon currents, wave motion, and capillary flow.

Once short-range attractive forces have brought the microorganisms very close to a suitable surface, many of the cells secrete extracellular organic polymers which serve to anchor them to the substratum.[8] This phase of biofilm formation is known as "irreversible sorption" since the bacteria now are permanently bound to the surface. The polymeric bridges between cells and substratum can easily be observed using scanning electron microscopy (Figure 2). As bacteria become more numerous and produce more extracellular adhesive material, living and dead cells become bound in the polymeric matrix, and a complex, dynamic fouling community of bacteria, algae, protozoa, trapped detrital material, and, eventually, macroorganisms develops (Figure 3). The rate at which the fouling layer builds up depends upon a number of environmental factors, including the chemistry, temperature, and velocity of the water. Stagnant conditions may be created by pits and crevices or by periodic shutdowns of pumping systems, leading to rapid accumulation of fouling organisms and their products.

Colonization of surfaces offers some advantages to marine microorganisms as the nutrient level of open ocean water often is too low to support active growth of many bacteria. Since nutrients tend to concentrate at interfaces, solid/liquid and liquid/air interfaces often provide the only sites where nutrient levels are adequate for microbial growth. Thus, microorganisms attached to surfaces are able to benefit from the enriched nutrient status there.[9] In flowing water systems (such as the surface of a ship's hull), attachment also ensures that organisms are not eliminated from that particular ecosystem and can continue to function in the fouling community.

Research during the past decade on marine biofilm formation has dealt mainly with the qualitative aspects of bacterial attachment to surfaces. Many studies have provided visual records of the attachment of various microorganisms to metallic and non-metallic surfaces in the sea,[10,11] but few efforts have been made to analyze natural biofilms more specifically.[12] Studies in this area often have used artificial seawater as the test medium. Evidence strongly suggests that results from experiments on marine biological fouling and corrosion differ when the analyses are conducted in natural seawater.

The development of methods for quantifying bacterial attachment and growth on metals has allowed researchers in our laboratory and others to investigate the attachment of specific marine bacteria to alloys of known composition. We have found that both the number and kind of bacteria that attach is a function of the type of metal and the way in which its surface was prepared. Copper-based alloys, for example, which have become attractive for seawater service because of their antifouling properties, are less rapidly fouled than other metals.

Figure 2

Scanning electron micrograph of a microcolony of marine bacteria on titanium that has been exposed to seawater for 96 hours. Note extracellular polymer material attaching cells to surface and to one another. Scale bar = 10μ.

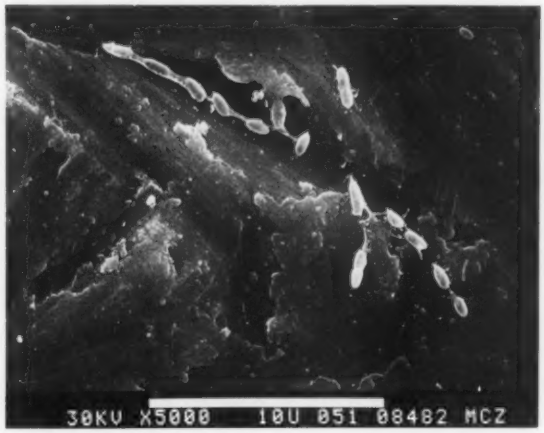
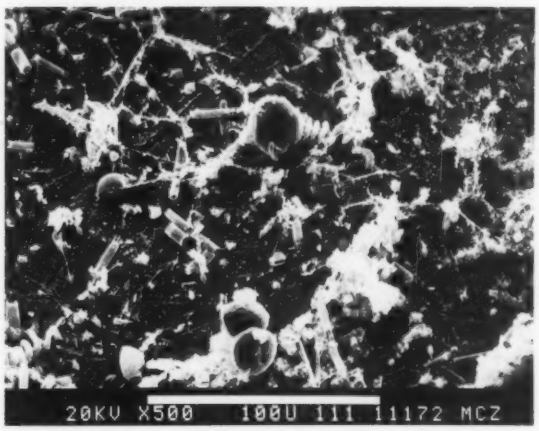


Figure 3

Seven-day old microbial film on 316 stainless steel, consisting of bacterial colonies, protozoa, diatoms, and detritus. Scale bar equals 100μ.



However, in terms of microbial attachment, they have no advantage over other alloys once the base metal surface becomes obscured by microbial polymers or corrosion product films. This implies not only that biofilm growth is sensitive to continuing changes in the nature of the metal surface, but also that few, if any, metals are immune to the influence of microorganisms upon their corrosion behavior.

Corrosion by Microorganisms

Microbial colonization of manmade structures in the sea frequently leads to undesirable practical effects. The presence of even a very thin biofilm can greatly impair the efficiency of heat exchanger systems.[13] Furthermore, the accumulation of surface-fouling microorganisms, their metabolic products and exo-polymers, trapped detritus, and other organic matter greatly changes the nature of a metal surface and affects both the kinetics and type of corrosion.

Metabolic processes occurring at metal interfaces have a significant effect on a variety of different corrosion reactions. Some of the basic mechanisms by which microorganisms initiate or accelerate corrosion include:[14]

1. production of corrosive metabolic products, such as acids or hydrogen sulfide;
2. formation of discontinuous deposits on the surface, resulting in differential aeration and concentration cells;
3. disruption of natural and other protective films;
4. breakdown of corrosion inhibitors and coatings;
5. depolarization of cathodic or anodic reactions.

Several specific forms of microbiologically induced corrosion are discussed in more detail below.

Anaerobic corrosion

The presence of extensive fouling communities on structures submerged in seawater can easily limit diffusion of oxygen to the surface of metals used in their construction. Although growth of microorganisms on surfaces sometimes acts to reduce corrosion by providing a continuous barrier to the diffusion of oxygen to the surface, this deficiency in oxygen supply may be responsible for the initiation of localized corrosion caused by differential aeration, particularly if the fouling has resulted in discontinuous deposits on the surface. Such corrosion cells can be set up by macrofoulers (such as barnacles and mussels), as well as by microorganisms.

Anaerobic conditions existing beneath microbial biofilms on metal surfaces in contact with anaerobic sediments at the bottom of ocean, in stagnant, nutrient-rich water in pipes, or in heavily polluted seawater may also stimulate the growth and activity of bacteria which live only in anoxic environments. Some of these anaerobic bacteria, such as those of the genus *Desulfovibrio* which reduce sulfate to form hydrogen sulfide, have been associated with extensive corrosion of a wide variety of metals in the sea. Usually the corroding metals tend to pit, resulting in local perforations. Accelerated corrosion of copper-nickel alloys, for example, has been observed in polluted, oxygen-deficient waters, and the regions of greatest attack generaly showed distinct biofilms. It appears that accelerated corrosion of these alloys resulted from anaerobic microbial processes within the biofilms, and pitting of the copper-nickel alloys could be correlated with bacterial production of hydrogen sulfide.[15] Sulfate-reducing bacteria are a particular hazard on oil tankers and in oil drilling equipment and pipelines. The sulfur compounds dissolved in crude oil provide excellent substrates for the growth of these microorganisms, and pitting corrosion is a major problem. Examination of the pits and analysis of the corrosion products on adjacent surfaces suggests that the accelerated attack occurs as a result of microbial activity.[16] Sulfate-reducing bacteria also initiate pitting corrosion of aluminum in seawater.[17]

Theories suggested to explain anaerobic bacterial corrosion have been summarized by others[14,18,19] and will not be described in detail here. The most popular theory used to explain microbially-mediated anaerobic corrosion of iron-containing metals is cathodic depolarization, which suggests that corrosion is enhanced by removal of the protective film of hydrogen by the hydrogen-oxidizing, sulfate-reducing bacteria:

metal surface

$$Fe^0 \rightarrow Fe^{2+} + 2e^- \text{ (anode)}$$

$$2H^+ + 2e^- \rightarrow H^2 \text{ (cathode)}$$

sulfate-reducing bacteria

$$4H_2 + SO_4^{2-} \rightarrow HS^- + 4H_2O$$

overall process

$$4Fe + SO_4^{2-} + 4H_2O \rightarrow FeS + 3Fe(OH)_2 + 2OH^-$$

The enzyme hydrogenase, synthesized by many species of *Desulfovibrio*, may be involved in the depolarization process, although some non-hydrogenase-producing strains of *Desulfovibrio* also appear to stimulate corrosion. The role of hydrogen-consuming bacteria other than *Desulfovibrio*, such as methane bacteria, as a cause of corrosion has not been explored. Other theories suggest that sulfides, mercaptans, and other bacterial products may control the rates of anaerobic marine corrosion processes. For example, Iverson[20] has proposed that the corrosion is caused by a highly corrosive extracellular product rather than by the removal of hydrogen.

Acid production

Among the wide range of microbial corrosion-causing reactions which can be expected to occur in the marine environment, the production of organic and inorganic acids by microorganisms is a major source of

corrosion. These acids have been shown to cause extensive corrosion of steel piping[21], damage coatings, and destroy concrete.[22] Despite the importance of microbial acids as corrosive agents, little is known about the environmental factors that control acid production on metal surfaces or the relationship between acid metabolism and specific forms of corrosion.

Organic acids are produced by a variety of microorganisms during the fermentation of organic substrates in anaerobic environments. They may be released in large quantities by most bacteria, fungi, and algae. The types and amounts of organic acids produced during microbial metabolism depend upon the kinds of organisms present and the substrate molecules available. Typically the resulting metabolites are a mixture of organic acids, consisting most commonly of acetate, formate, lactate, propionate, and butyrate. The acids produced by these fermenting microorganisms may be used, subsequent to their release, as energy sources by other members of the community, perhaps yielding new metabolites that also are corrosive.

Very strong mineral acids are produced by other bacteria, which grow in aerobic habitats. For example, sulfuric acid is produced by members of the genus *Thiobacillus*, which generate energy for growth by oxidizing reduced sulfur compounds:

$$S^0 + \frac{3}{2}O_2 + H_2O \rightarrow H_2SO_4$$

These bacteria are the organisms primarily responsible for the extremely acidic conditions (pH 2–3) found in mine drainage waters.[23]

The sulfur-oxidizing bacteria typically coexist with the anaerobic sulfate-reducing bacteria, suggesting the possibility of synergistic effects from the metabolic activities of the two types of microorganisms. Sulfide produced under anaerobic conditions may be oxidized to sulfuric acid by *Thiobacillus* whenever oxygen enters the system.[24] It is commonly observed that stimulation of corrosion occurs when metals under anaerobic conditions are exposed to the air or to fresh, turbulent seawater. The degree of corrosion acceleration depends on the length of exposure to anoxic conditions prior to reexposure to aerobic conditions. Apparently the oxidation/reduction cycle between the two populations of bacteria, combined with the production of hydrogen sulfide, provides a mechanism for continuous corrosion and causes very rapid pitting of the metals. This effect of fluctuating oxygen concentration on corrosion has serious implications for metal structures which are exposed to turbulent seawater conditions or are periodically submerged and then reexposed to the air.

Hydrogen embrittlement

Hydrogen embrittlement is weakening of a metal resulting from the absorption of atomic hydrogen. In susceptible metals this results in a loss of ductility and tensile strength and often in premature failure of the material. This phenomenon is especially important in high-strength steels, although other alloys also are susceptible.[25] It consititutes a serious hazard, since catastrophic failures can occur with no prior warning. It is believed that microorganisms can play a significant role in hydrogen damage processes, and several mechanisms may be involved.

It is well established that external hydrogen gas can cause embrittlement in a variety of materials, including steels, titanium alloys, and nickel alloys.[26] A wide range of bacteria produce molecular hydrogen as an end product from the fermentation of carbohydrates. When this hydrogen is produced by organisms within the biofilm on a metal surface, it may under certain conditions be absorbed into the metal if dissociation into atomic hydrogen occurs.[27] Furthermore, acid production by fouling microorganisms may influence hydrogen embrittlement. Not only can the pH change associated with acid production affect surface conditions relevant to hydrogen entry into the metal, but also reduction of microbially derived protons (H^+) may be coupled to anodic dissolution of the metal, resulting in the formation of hydrogen atoms. If recombination of this atomic hydrogen into molecular hydrogen is prevented (by sulfides or other hydrogen evolution poisons), then the uncombined hydrogen atoms accumulate at the metal surface, and the probability of their absorption into the metal lattice increases. Alternatively, bacteria which consume hydrogen during the fixation of carbon dioxide (e.g. *Desulfovibrio* species) may actually suppress the absorption of hydrogen by removing it from the metal surface before it diffuses into the metal itself.

Certain substances such as sulfide ions, phosphorous-containing ions, arsenic compounds, and cyanides are known to be effective poisons of the conversion of atomic to molecular hydrogen. In the presence of such compounds, uncombined hydrogen atoms increase in number on metal surfaces, and hence the probability that they will be absorbed into the metal also increases. Many of these poisons are found in petroleum process streams, which is the reason that hydrogen damage of metals is a major problem in the petroleum industry.

Hydrogen sulfide (H_2S) production by sulfate-reducing bacteria in anaerobic marine environments thus may stimulate the absorption of atomic hydrogen into metals by preventing its recombination into hydrogen gas. As described before, these nearly ubiquitous microorganisms are active in the anoxic conditions existing beneath microbial biofilms on metal surfaces, inside tubercles or under deposits, in crevices, on metals surfaces, in contact with anaerobic muds or sediments, and in stagnant, polluted waters. Whenever atomic hydrogen is produced by proton reduction in the presence of H_2S,

embrittlement of sensitive materials must be expected. H_2S produced in aqueous environments does, in fact, limit the use of hardened, high-strength steels in oil and gas equipment and in sour gas wells. Embrittlement and failure of offshore structures might be expected to occur at the sediment-water interface, where H_2S production by sulfate-reducing bacteria is greatest. Use of materials which are sensitive to hydrogen should also be discouraged in waters heavily polluted by organic matter.

Metal oxidation

In well aerated seawater, the corrosion of alloys containing iron and manganese is common. The presence of microbial films on surfaces provide the potential for oxidation of iron and manganese by iron and manganese bacteria. A number of iron bacteria have been associated with corrosion processes,[28] including members of the genera *Gallionella*, *Sphaerotilus*, and *Siderocapsa*. These bacteria often are associated with the formation of ferric and manganic oxide tubercles seen on steel surfaces. The deposits may contain corrosive metal chlorides, and sulfate-reducing bacteria often predominate inside the tubercles, where oxygen transfer is inhibited. Other organisms which may be involved in the corrosion of iron include *Thiobacillus ferrooxidans*, which obtains its energy for growth from the oxidation of ferrous iron, but the importance of these bacteria in marine corrosion is not known.[24] Also, little information is available about the role of manganese-oxidizing microorganisms in mediating corrosion reactions.

In recent years, the study of stalked and filamentous metal-oxidizing bacteria has progressed significantly. New marine organisms have been isolated which are capable of oxidizing manganese or iron. Studies of ocean floor manganese nodules have yielded a complete family of bacteria capable of oxidizing manganous compounds.[29] Fungi may also be involved in the formation of organic iron and manganese complexes. No attempt has been made to determine the function of these unusual microorganisms in corrosion processes.

Marine engineers are encouraged to consider biological factors when making designs, choosing materials, and performing corrosion tests. In particular, the importance of using fresh, natural seawater for corrosion testing cannot be overemphasized. Although conventional marine corrosion studies often use either artificial seawater or aged, sterilized seawater, it is impossible to assess the importance of the marine microflora in studies of this kind.

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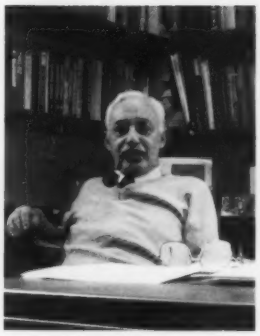

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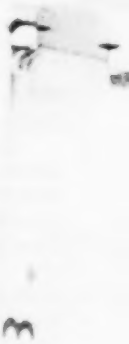
Marianne Walch, a Maryland native, received her B.S. in microbiology from the University of Maryland in 1980 and her master's degree from Harvard University in 1981. Currently she is completing a doctoral thesis at Harvard on bacterial corrosion of metals.

High Pressure at 10,000-Times Faster Rates

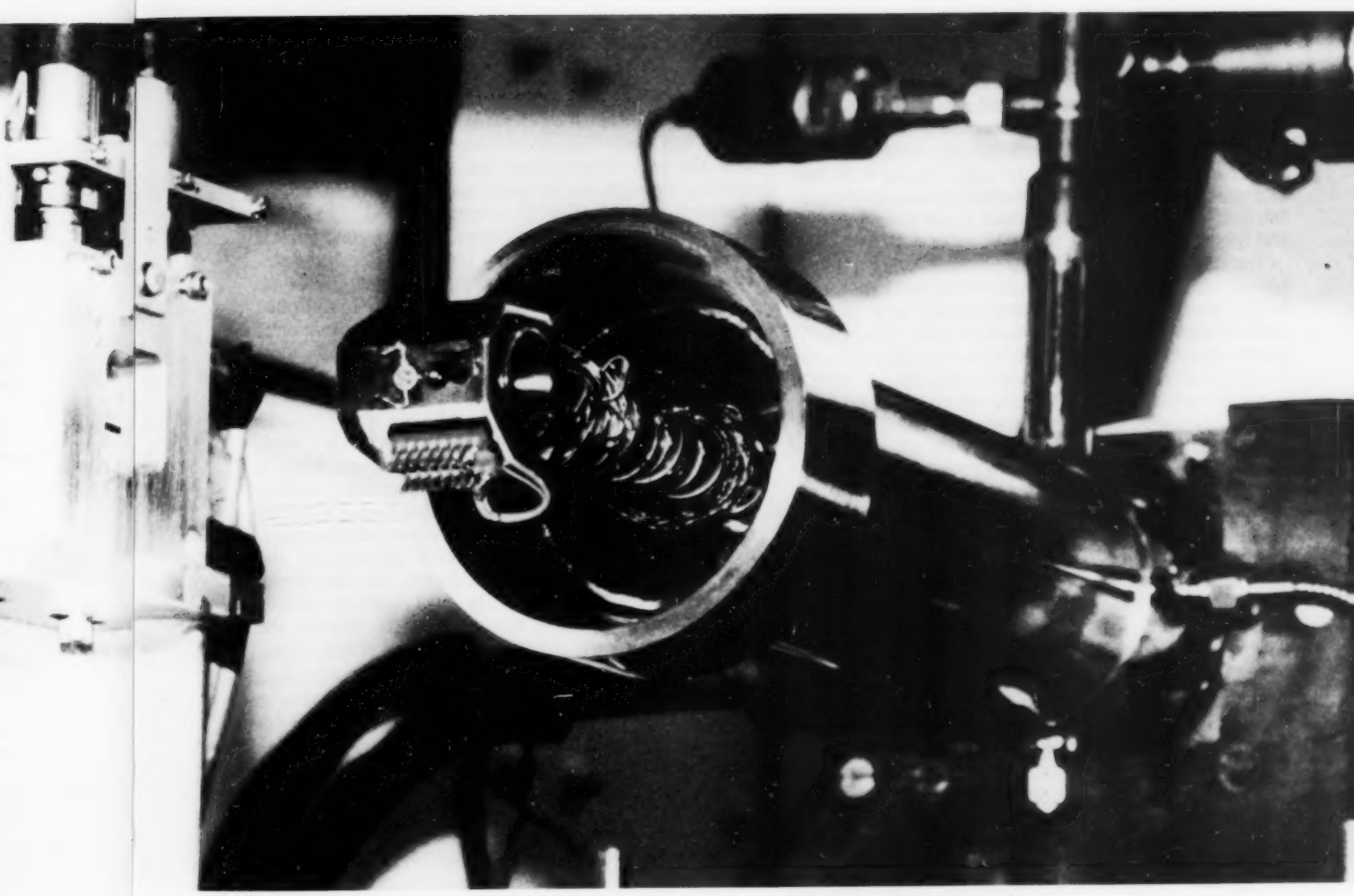
by E. F. Skelton
Naval Research Laboratory



Pressure is an extremely important thermodynamic variable, both in terms of understanding physical properties of materials and in the fabrication of new forms, or polymorphs, of existing materials for naval and other DoD applications. Diamond and cubic-boron nitride represent classic examples of useful polymorphs which can only be produced in a high pressure environment. Pressure also provides the most efficient means of altering interatomic dimensions, one which does not necessarily affect other physical properties, such as thermal energy or chemical environment. Its role, such as in understanding the origin of the newly discovered superconductivity in organic charge transfer salts based on the cation molecule ditetramethyltetraselenaful-valenium (TMTSF), would appear to be critical since all but one of these salts are superconducting only at elevated pressures.

More specifically, most modern physical theories are based on atomic force models which depend, in turn, on relative interatomic separations and crystallographic arrangements. Although temperature can be used to alter these parameters, the temperatures which can be routinely achieved in research laboratories today are roughly an order of magnitude less effective than pressures which can also be readily attained. Moreover pressure can be applied in such a way as to leave the thermal energy of the system invarient, thereby simplifying the interpretation of any resulting changes. For example, changing the temperature of most materials by, say one thousand degrees (C or K), which can easily be done in the laboratory, will produce a fractional change in length of a few tenths of a percent; on the other hand, pressures of a few hundred thousand atmospheres, which can also be routinely generated in the laboratory, will cause most materials to undergo fractional length changes of several percent.

re Structural Data



Diamond-anvil pressure cell

High pressure structural studies are important not only to test various physical theories and thereby improve our theoretical understanding of solids, or to map out phase diagrams in pressure, volume, temperature (P,V,T)-space, but in terms of producing new, and possibly better materials as well. As noted above, it is not necessarily the atmospheric form of a substance which is the most useful from a utilitarian point of view. Nb_3Si is another example where pressure has been effective in producing a new and better polymorph. Empirical arguments have suggested that if this material could be formed in the cubic, A15-structure, rather than its normal tetragonal, Ti_3P-phase, it would exhibit superior superconducting properties. Recent ultra-high pressure shock treatments have been successful in producing such a metastable transformation. In transforming from the Ti_3P-phase to the A15-phase, the superconducting transition temperature of Nb_3Si has been raised from 0.29K to 18.5–19K.

A similar example which is presently being tested is MoN. Theorists at the Naval Research Laboratory (NRL) have predicted that MoN would be a high T_c superconductor, if it could be formed in the Bl or NaCl-crystal structure.[1] Stiochiometric MoN normally forms in a hexagonal lattice, the so-called delta-phase, with a calculated mass density of 6.9 gm/cm. Based on extrapolated properties of similar materials, it is expected that if this material were to transform to the Bl-structure, then there would be about 23 percent increase in the density, thus suggesting that the Bl-phase would be favored at elevated pressures. Experiments to test this theory are presently underway at NRL.

In attempting to learn more about materials and their physical properties, it is important not only to identify the critical thermodynamical coordinates, but to monitor from a crystallographic or structural point of view how materials transform from one phase to another — transition kinetics. It is with information of this type that scientists will be able to predict which factors are important in terms of inhibiting reverse transitions, so that, if discovered, a desirable high pressure polymorph may be retained under atmospheric conditions. Until recently, such information has been very difficult to obtain, but, as discussed below, the extreme spectral brilliance of synchrotron radiation is changing this.

Four years ago, with direct support from the Material Sciences Division of the Office of Naval Research (ONR), a team of NRL scientists initiated a program at the Stanford Synchrotron Radiation Laboratory (SSRL) to assess the feasibility and possible advantages of performing high pressure, variable temperature experiments with a synchrotron radiation (SR) source. New vistas in high pressure materials research have opened as a result of this work. It has been demonstrated that structural data can now be acquired from a high pressure environment at rates many orders of magnitude faster than heretofore possible. Also the kinetics of pressure, temperature (P,T)-induced phase transitions can be studied in time frames which were unfathomable before; and pressure related studies which might otherwise be prohibitive, due to the extended time requirements of data collection, are now feasible. Details of this program are described in this article.

Diamond-Anvil Cell (DAC)

Until the mid-1960's, virtually all high pressure research was carried out in massive hydraulic presses. But, over the past fifteen years, the field has been revolutionized through the creation and development of the diamond-anvil cell (DAC). A variety of DAC designs are now in existence. They all share certain fundamental properties; that is a mechanism for aligning both the surface faces and the axes of a pair of gem quality diamond anvils and bringing these anvils together in a controlled manner. Since the working surface area of the anvil faces is kept small (*ca.* <1 mm^2), modest loads, usually generated by hand, can be used to routinely produce pressures of tens of GPa;* the current accepted static pressure limit being 172 GPa.[2]

The DAC can be used either with or without a hardened metal gasket between the diamond-anvils. When a gasket is employed, it forms the pressure chamber (Figure 1) and provides a means of producing a hydrostatic, or quasi-hydrostatic pressure environment, depending on the pressure range of interest and the hydraulic fluid used. Without a gasket, the sample will extrude out the periphery of the anvil interface until its internal frictional forces are sufficient to contain the sample. In this case, the pressure will vary from a maximum near the center to atmospheric at the periphery.

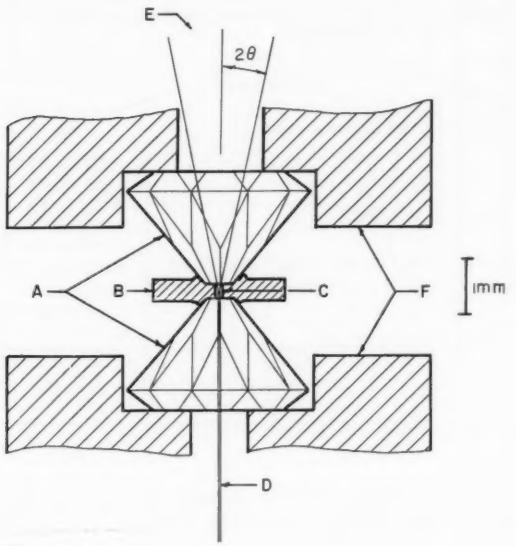
The pressure is generally measured by including a pressure calibrant with the sample(s) of interest. Materials for which the equations of state are reasonably well known are often used (Cu, Ag, Au, NaCl, or CsCl). The calibrated pressure shifts in other known measurable properties can also be used, such as the wavelength dependence of the optical fluorescence radiation from ruby or the superconducting transition temperature of Pb or Sn.

The DAC has three important advantages over the older, comparatively large volume and more massive high pressure systems: simplicity, compactness, and transparency. Because of its miniature size, the DAC can be readily transported from laboratory to laboratory, as well as operated in a variety of special environments. This

*The S.I. unit of pressure, the Pascal (Pa), is defined to be 1 NM^{-2}; thus 10^5 Pa = 1 bar = 0.9869 atm. = 1.0197 kg cm^{-2}; 1 GPa = 10 kbar = 145,038 psi.

Figure 1

Schematic drawing of a typical diamond-cell showing the diamond-anvils (A), gasket (B), pressure chamber (C), incident (D) and scattered (E) radiation paths, and hardened tungsten carbide support surfaces (F). (Mechanism for advancing diamonds and thus generating pressure is not shown.)



feature also allows the DAC to be cooled or heated, as necessary, with relative ease. At one extreme, temperatures of several thousand degrees C have been attained with pulsed laser heating techniques; at the other extreme the world record of highest pressure and lowest temperature was achieved several years ago at NRL by coupling a DAC to a He^3–He^4 dilution refrigerator. The apparatus was pressurized to 10 GPa and simultaneously cooled to 30 mK. The most important advantage of the DAC, however, is the relative transparency of the diamonds to a wide range of electromagnetic radiation. Thus Brillouin and Raman scattering experiments, as well as optical absorption and reflection measurements, can all be performed as a function of both pressure and temperature. But, of even greater importance perhaps, is the fact that x-radiation may be brought to and from the pressure chamber with relatively little attenuation; as a consequence, today the DAC is the most extensively used instrument for pressure dependent structural studies. The design, development, and application of DAC to high pressure research have recently been reviewed.[3]

X-Ray Diffraction with the DAC

Although a few cells have been designed and fabricated for single crystal studies, the vast majority of high pressure x-ray experiments are performed with polycrystalline or powder samples, usually employing photographic measurement techniques. In most cases, the sample chamber is illuminated with filtered radiation from a sealed beam x-ray tube, and the forward scattered radiation is photographically recorded over a range of diffraction angles, usually from $\pm 20°$ to $\pm 30°$ in 2Θ. Thus a portion of a Debye-Scherrer photograph is produced as a function of pressure. Some researchers have replaced the film cassette with a position-sensitive photon detector, thus producing the electronic equivalent of a powder photograph.

Although the dimensions of the pressure cavity tend to vary somewhat for each experiment, depending, *inter alia*, on the scattering power of the sample and the pressure range of interest, typical sizes for the cylindrical pressure chamber (height and diameter) are in the 100 μm range. This results in a working volume on the order of 10^{-3} mm^3 which must contain the sample, pressure calibrant, and hydraulic fluid (if used). A consequence of this is that when conventional radiation sources are employed, extended exposure times are usually required before useful structural data can be obtained. As an extreme example, in a series of pressure calibration measurements on four elemental metals (Cu, Mo, Pd, and Ag), using both Mo K α (Zr β-filtered) and AgKα (Rh β-filtered) radiation, exposure times ranged from 100 to 400 hours.[4] Although the necessary exposure period will vary from experiment to experiment, tens to hundreds of hours of exposure are not uncommon when using conventional x-ray sources and film techniques.

Energy Dispersive X-Ray Diffraction

It was first demonstrated at NRL that the rate of acquisition of structural information from a DAC could be accelerated by utilizing the higher energy x-ray photons available in the bremsstrahlung of an x-ray tube (frequently a tungsten-target tube is used because of its more uniform heterochromatic radiation content) and analyzing the scattered x-ray photons under conditions of fixed geometry in terms of their respective energies, so called, energy dispersive x-ray diffraction (EDXD).[5]

The Bragg relation specifies the conditions which must be satisfied for a diffraction event to be possible, *viz.*:

$$\lambda = 2\, d_{hkl} \sin \Theta \qquad (1a)$$

or

$$E\, d_{hkl} \sin \Theta = \frac{hc}{2} \qquad (1b)$$

where d_{hkl} is the spacing between the (hkl)-crystallographic planes, Θ is the Bragg diffraction angle,

h is Planck's constant, c is the speed of light, and λ and E are the x-ray photon wavelength and energy, respectively. In angular dispersive diffraction, λ is fixed, usually at one of the characteristic wavelengths emanating from an x-ray tube, and Θ is scanned to obtain d-spacing and other structural information. Alternatively in EDXD, Θ is fixed and E is scanned, usually with an energy sensitive photon detector, to obtain the equivalent information.

Need for Synchrotron Radiation

By employing EDXD methods and sealed beam radiation sources, exposure times required to obtain structural information from the high pressure environment are generally reduced; replacement of the conventional x-ray tube by a rotating anode source results in a further improvement, but measurement periods are still prohibitively long in many instances. An obvious and very significant advancement can be achieved by performing these high pressure experiments instead with a synchrotron radiation (SR) source. NRL scientists performed a recent comparison between the spectrum available on the SSRL heterochromatic beam line (II–4) (corrected for various absorbers in the beam line) and that available from a conventional, tungsten target x-ray tube; the results are shown in Figure 2.[6] Clearly, over most of the useful energy range (from about 10 to 60 keV), there are more than six orders of magnitude more photons available from the SR source.

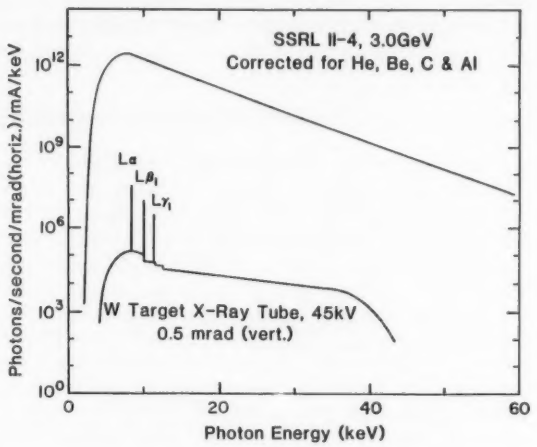
Other noteworthy advantages of the SR source over conventional sources include improved beam divergence and a well known energy-intensity profile. The beam divergence of a conventional radiation source is generally large, and the experiment is often performed close to the source point usually within several cm. In contrast, the divergence of the typical SR beam is in the mrad range and the experiment is usually located several decameters from the source point. Thus a highly collimated beam is available for EDXD experiments. The intensity-energy profile of the SR-source is smoothly varying and well known, whereas the bremsstrahlung from an x-ray tube is more difficult to evaluate and complicated by the presence of characteristic lines.

Experimental Set-Up

The experimental set up and operational procedure for EDXD with a DAC are relatively straightforward, thereby simplifying transferral to a SR experimental station. Because of the compactness and transportability of most of the components, the equipment can be assembled and aligned at the home laboratory and then transported to the SR-site. The DAC is centered in the SR beam and

Figure 2

Comparison of the energy-intensity spectrum available from SPEAR at SSRL (corrected for various absorbers in the beam path) with that available from a typical tungsten target x-ray tube (Reference 6).



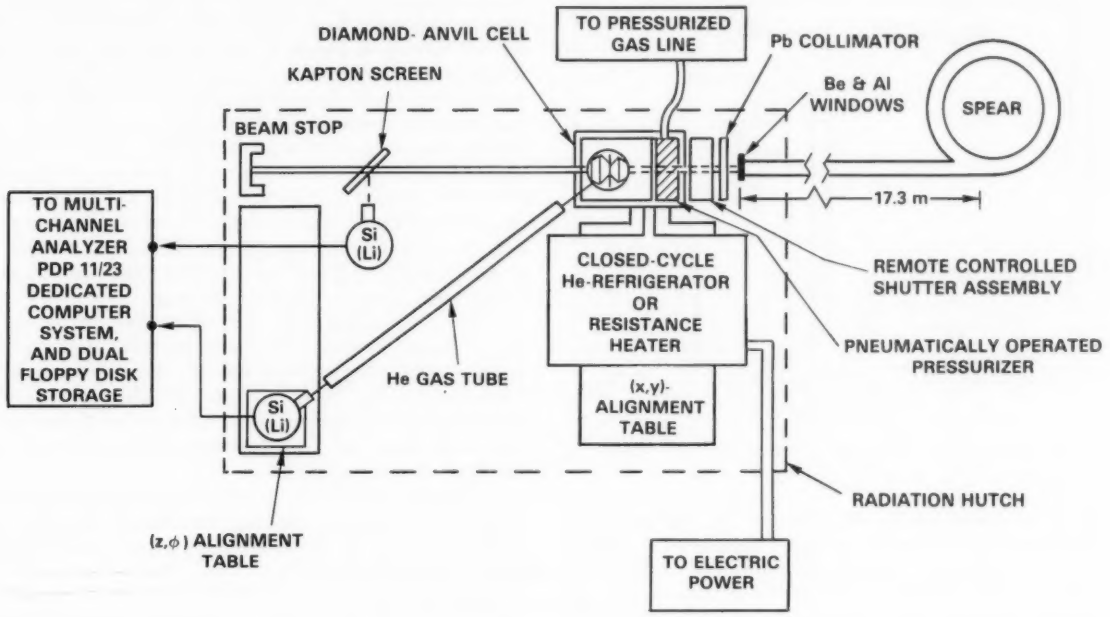
an energy sensitive photon detector is fixed at some, usually, low 2Θ angle. (Figure 3). Li-drifted Si- and Ge-detectors and intrinsic Ge detectors have been used as energy sensitive photon detectors.[7]

The lower limit of usable photon energies for EDXD with a DAC is determined predominantly by the low energy absorption properties of the diamond-anvils and, of course, the sample itself. Usually data are collected above 10 keV. The upper limit is determined by two factors, the number of available high energy photons in the SR-beam and the efficiency of the detection system. The former is determined by the radius of the synchrotron ring and the orbiting electron energy[8], and the latter is controlled by the stopping power of the detection crystal. The efficiency for most Si(Li) detectors falls below 20 percent above 60 keV, whereas that for the intrinsic Ge-detectors generally remains high (>80 percent) up to 100 keV. However, spectra recorded with Ge detectors are usually complicated by the presence of escape peaks. Most reported high pressure EDXD SR spectra lie in the 10 to 60 keV range.

The resolution of EDXD-peaks, defined as the full-width at half-maximum, is determined by two factors: (1) the resolution of the energy sensitive detector and associated electronics and (2) that due to geometrical factors (beam divergences and finite slit widths). Typically, with solid state detectors, the energy resolution will degrade from about 3 percent near 6 keV to about 9 percent near 45 keV.

Figure 3

Schematic drawing of a variable temperature energy-dispersive x-ray diffraction set-up with a diamond-anvil cell on a heterochromatic beam line (References 7 and 14).



An EDXD spectrum of $Ce_{.8}Th_{.1}La_{.1}$ and NaCl pressure calibrant recorded at a pressure of 0.5 GPa, a temperature of 60K, and a diffraction angle of 13° is shown in Figure 4. In addition to the diffracton peaks as distinguished by the assigned Miller indices in the figure, there are also a number of fluorescence peaks in the spectrum arising from the rare-earth elements in the sample. Although these cannot be avoided, possible interference between diffraction and fluorescence peaks can usually be eliminated through small changes in 2Θ since the latter are invariant to changes in the experiment geometry; whereas the diffraction peaks will shift as required by equation (1b).

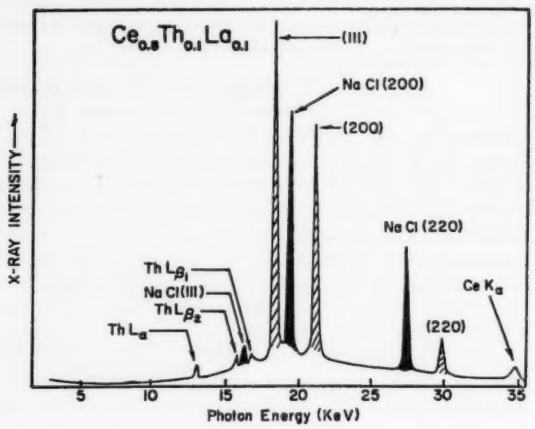
When conventional radiation sources are used because of the extended time required for each recording, it is usually acceptable to change the force on the diamonds and hence the pressure, manually. However, for safety reasons when using SR, the equipment is generally secured in a radiation-proof container (hutch), and access can often take several minutes or more. It is therefore desirable to provide some means of remotely varying the pressure. By introducing well developed capabilities for heating and/or cooling the pressure changer, it is also possible to remotely control and vary the sample temperature. Thus the assemblage provides an excellent tool for rapidly obtaining structural information throughout (P,T)-space.

Speed of Data Acquisition

The question naturally arises as to how rapidly EDXD spectra can be obtained with this method? The answer will depend on a number of factors: the photon-flux available at the scattering center, the scattering power and size of the sample, and the collection and analysis efficiency of the detection/analysis system.

Figure 4

Diffraction spectrum of $Ce_{.8}La_{.1}Th_{.1}$ recorded at a pressure of about 0.5 GPa, a temperature of 60 K, and a diffraction angle of 13° (Reference 14).



However, based on a large number of high pressure experiments with a wide variety of specimens at SSRL, with the synchrotron running at from 3.0 to 3.5 GeV, and beam currents ranging from 100 to 20 ma, spectra of acceptable quality can usually be acquired in a matter of minutes, *e.g.* the spectrum in Figure 4 was recorded for 100 sec.

In a specific timing study, monitoring the NaCl-(200) pressure calibration peak, for which about 500 counts were recorded each second, the standard deviation in the measured area under the peak (integrated intensity) degraded from less than 1 percent for extended measurement periods (>5 min) to about 3 percent for 10 sec. scans. The precision in the experimental determination of the peak energy was better than 0.01 percent for extended scans and degraded to about 0.04 percent for 10 sec. scans.

Phase Transitions: Structural

One of the most extensive uses of the DAC has been for the study of pressure-induced phase transitions. Such studies are ideally suited for EDXD measurements with SR because of the rapidity with which the critical thermodynamic transitions coordinate(s), pressure and/or temperature, can be identified. Often the more intense EDXD peaks in the initial phase can be monitored as the thermodynamic variable(s) is (are) changed until the transition is initiated. Then, as the EDXD peaks of the initial phase begin to lose intensity with the concomitant growth of the EDXD peaks of the new phase, the dynamics of the transition can also be measured.

An example of a pressure-temperature activated transition is the Bl(NaCl-structure)-B2(CsCl-structure) phase transition which occurs in many alkali-halides. This transition for KI is sluggish and is represented by the EDXD spectra in Figure 5. On the left side, the room temperature EDXD spectra are plotted as a function of increasing pressure from 0.83 GPa to 3.17 GPa. Below the transition pressure of 1.8 GPa, only the (200)-peak of the Bl phase is present at about 22 keV; at 1.8 GPa the material enters the two-phase region and the (110)-peak of the B2-phase is also present at about 25 keV. Further increase in pressure and the transition is completed as evidenced by the disappearance of the (200)-peak. The third strong peak above 26 keV is the NaCl-(200) peak which, in this case, serves as the pressure gauge.

The reverse transition is demonstrated on the right side of Figure 5 where spectra were recorded at increasing temperatures as the pressure was held approximately constant at 1.5 GPa. The KI sample is initially in the two-phase region and remains there until the temperature is increased above 100 C, whereupon conversion back to the Bl-phase is completed.[9]

Another example of how SR has aided in unraveling a particular pressure induced reaction is provided in CuBr. Several years ago in searching for the possibility of high T_c superconductivity in CuCl, researchers in NRL obtained only very tenuous evidence to support an alternative explanation, a pressure induced Guinier-Preston transitional precipitate disproportionation reaction: $2\ CuCl \rightarrow Cu + CuCl_2$.[10] Due largely to the more brilliant SR-source, recent experiments at SSRL have provided *prima facie* evidence of this reaction in the isomorphic compound CuBr.[11]

Phase Transition: Kinetics

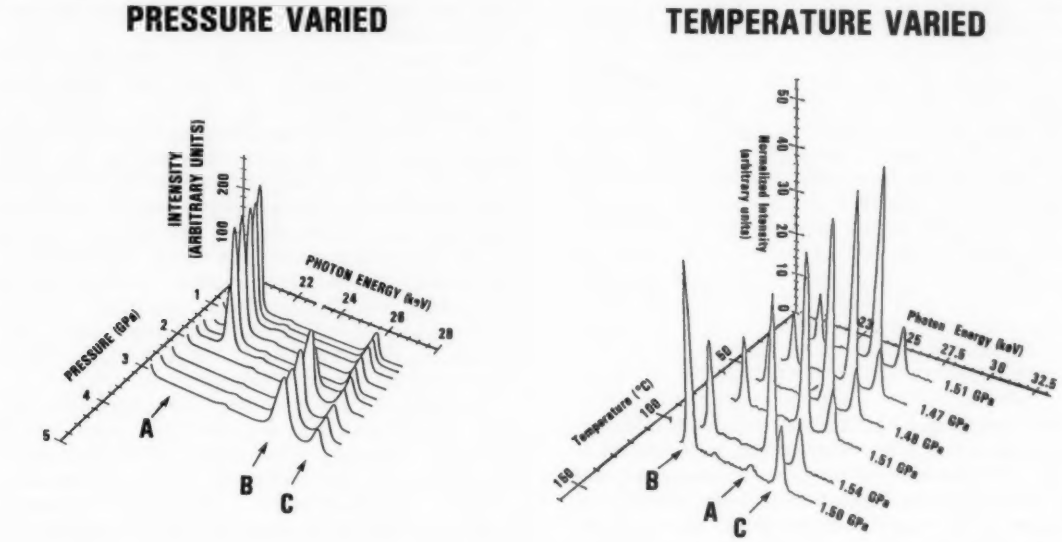
An example of phase transition information which could not be obtained from a DAC without the high speed data made available with the SR-source is provided by the B1–B2 transition in KBr. If, as is the case here, the structure of each phase of a two component system is known, then intensity data from any pair of peaks in each of the respective phases can be used to determine the volume fraction of each phase. For certain isothermal phase transitions involving nucleation and growth processes, it is expected that the time dependence of the growth of the new phase can be represented by the Avrami equation, viz.:

$$V(t) = 1 - \exp(-kt^n) \qquad (2)$$

where V(t) represents the time dependence of the volume fraction of the new phase, k is the growth rate constant,

Figure 5

Diffraction spectra showing pressure and temperature induced B1–B2 phase transitions in KI (Reference 9).



A = KI-(200) peak, B1 phase
B = KI-(110) peak, B2 phase
C = Na Cl calibrant (200) peak

and n the exponential time constant. Data taken for the KBr transition at a pressure of about 2 GPa are plotted in Figure 6; the straight line is predicted by equation (2); and the slope and intercept provide values for the rate parameters appropriate to such a transformation.[7]

It is to be noted that this information could not have been obtained from the DAC without the SR-source. In this case, the greater part of the transformation was completed during the first five hours. If data were collected over periods of hours, as would be necessary with a conventional radiation source, instead of the seconds or minutes possible when SR is used, each spectrum would of course represent a time average over that period and hence over the two respective phases. Thus the ability to obtain structural information from the sample during the phase transition is critical.

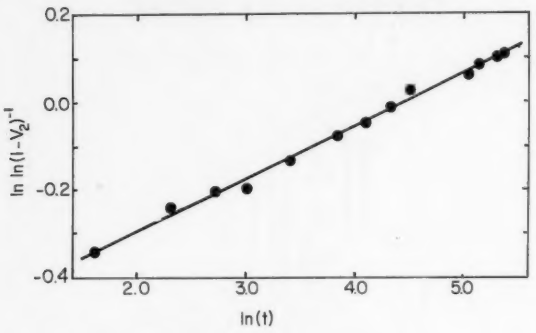
In the most recent series of experiments at SSRL, another significant improvement has been made in the rapidity of acquiring data. Rather than measure the entire EDXD spectra as a function of time as a transformation is taking place, specific diffraction peaks are isolated, such as the peaks from the B1 and B2 phases in Figure 5 and the multichannel analyzer, which is normally used to record the entire spectrum, is converted to operate in a multi-channel scaling mode. In this mode, the integrated EDXD intensity of the isolated peaks is recorded for a preset period of time. This dwell time can be set as short as 1 msec. and is adjusted to be compatible with the particular transition being studied. Thus transitions of msec. duration can be studied; efforts are presently underway to extend this into the μsec-range.

Variable Temperature Studies

Because of its compact size, the DAC can readily be heated or cooled to permit measurements at simultaneous extreme pressures and temperatures. One program underway at SSRL by a collaborating team of scientists from NRL and the Universities of Hawaii and Chicago involves cross-calibration of the two high pressure

Figure 6

Kinetics of the isothermal growth rate of the high pressure phase of KBr (Reference 7).



calibrants, NaCl and Au. To test existing equation-of-state calculations, it is necessary to span large regions of P,T-space. If conventional methods were employed, this would be a very time consuming process; however, by employing a SR-source, results have already been reported at P,T limits to 9 GPa and 550K, respectively.[13]

Very recently, NRL scientists, with support from colleagues at the University of California at Los Angeles and Los Alamos National Laboratory, have performed the first high pressure, low temperature experiments on a SR-source.[14] Specifically a specially designed Be-Cu DAC has been coupled to a helium closed-cycle refrigerator and remotely operated to 40K. The equation-of-state calculations of NaCl have also been extended from 298 to 0K in order to provide a low temperature high pressure calibrant.

The first application of this low temperature system was to study the first- and second-order phase transitions in a variety of Ce-based rare earth compounds. These materials are of interest because of the two critical points which are now known to exist in the P,T-phase field. More specifically, the diagram of $Ce_8La_1Th_1$ exhibits a first order γ–α transition line that terminates in a critical point, completely analogous to a gas-liquid condensation. The two phases are isomorphous, both being FCC-structures; however, there is about a 15 percent decrease in the volume on going from the γ-phase to the α-phase.

The addition of rare-earth impurities to the Ce-Th alloys simulates "negative" pressure and leads to the disappearance of the first-order transition at ambient pressure. This "negative" internal pressure can be compensated by the application of external pressure, resulting in the "re-entrance" of a first-order transition and the appearance of two critical points at either end of the first order transition line.

A typical EDXD spectrum of a mixture of $Ce_8Th_1La_1$ and NaCl is shown in Figure 4. The three prominent diffraction peaks centered near 20 keV photon energies were used for the actual measurements; the NaCl-(200) peak served as the internal pressure calibrant. Several fluorescence peaks arising from the sample are also seen in the spectrum.

The effect of moving through the lower critical point is represented in Figure 7; the measured temperature dependence on cooling of the $Ce_8Th_1La_1$ unit-cell parameter is plotted along the atmospheric pressure isobar (crosses) and with increasing pressure to 1.3 GPa (circles). Along the isobar, the sample is below the lower critical point and the approximately 1 percent volume decrease represented in the figure is due solely to thermal contraction. When the sample is cooled and simultaneously pressurized, the sample is above the lower critical point and the γ–α, first-order phase boundary is crossed as evidenced by the volume decrease of more than 11 percent in going from 0.4 GPa, 220 K to 0.8 GPa, 170 K, points A and B, respectively, in Figure 7.

Research on this interesting phase transition continues; the objective is to map the P,V,T-phase field of $Ce_8Th_1La_1$, especially in the vicinity of the two critical points. It is noted that each of the 23 data points shown in Figure 7 was recorded for 5 minutes; this represents less than 2 hours of measurement time. If conventional facilities had been used, it would have required more than one month of continuous operation to obtain the same information.

Large Volume Systems

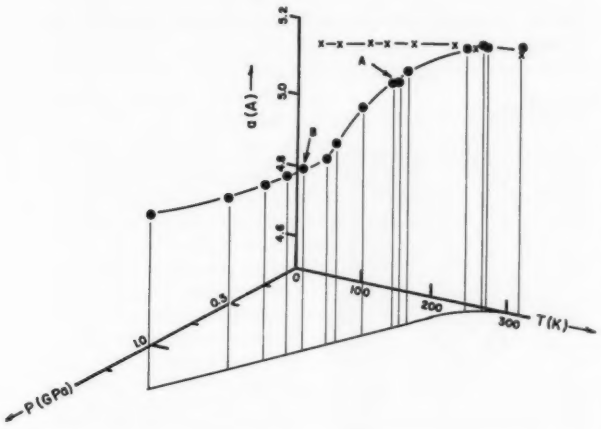
As noted above, originally all high pressure research was pursued in comparatively large volume systems: piston-in-cylinders, supported anvils, or a variety of multiple anvil devices. However, the extraction of information from the high pressure environment in these systems is complicated by the variety of absorbing materials separating the pressure chamber from the laboratory. In a few instances, x-ray tubes were successfully interfaced to these large volume systems, and *in situ* diffraction data were obtained from the high pressure environment, albeit at usually a rather lethargic pace.

Despite the enormous success and advantages of the DAC, a need remains for these large volume systems. An example would be to study and perhaps optimize the production parameters for pressure synthesized materials, such as diamonds and cubic boron nitride.

A Japanese team has taken the lead in this area by recently installing a 500-ton uniaxial press on one of the beam lines at the Photon Factory, recently completed Japanese synchrotron. The internal assemblage consists

Figure 7

Effect of increasing pressure on the temperature dependence of the unit cell parameter in $Ce_{.8}Th_{.1}La_{.1}$ (Reference 14).



of a cubic-anvil system which can produce pressures up to 10 GPa in a volume defined by 4 mm edge, tungsten carbide anvils. The entire system can be translated in any of three orthogonal directions, so that the scattering center can be adjusted relative to the SR-beam. Data can be recorded in either an energy or angular dispersive mode; the detector can traverse an angle of ±35°.

Another important advantage of these large volume systems is that much higher temperatures can be achieved since diamond anvils are not employed. The Japanese press can be operated to temperatures of 1700 C, whereas DAC's are usually kept below 600 C to avoid graphitization of the anvils.

This author recently had the unique experience of being the first non-Japanese scientist to perform experiments on the first Japanese hard x-ray synchrotron at the The Photon Factory, located at the Japanese National laboratory for High Energy Physics in Tsukuba. A detailed report of that work will be published in the ONR-Far East *Scientific Bulletin*.[15]

Future Directions

There seems little doubt that as SR sources continue to become more available to the research community, the number of groups seeking to employ their superior properties for high pressure research will grow. For example, with direct support from the National Science Foundation, there is a program underway by researchers at the Universities of Hawaii and Washington and the Naval Research Laboratory to instrument a beam-line at SSRL with the necessary electronics and detection equipment to provide users with the necessary apparatus for EDXD experiments. When this is operational, users will need only to bring their DAC's, perhaps already loaded and pressurized, in order to perform high pressure structural studies.

A natural quest for many high pressure researchers is for higher and higher pressures. One means of achieving this end is through the use of smaller and smaller contact areas; scientists at Cornell University have recently been using 25 μm diameter gasket holes and, in a separate arrangement, diamond-indentors with contact areas of only 1.6 μm diameter. With the concomitant diminishing sample volume, future researchers will need not only an SR source, but the added brilliance of the radiation from wiggler lines in order to extract a measurable signal from the sample in a reasonable time. Moreover, given the accelerated rates of data collection and the increased use of microprocessors in data acquisition and analyses, it is reasonable to also employ these microprocessors for controlling the P,T-variables.

This should ultimately lead to better resolution in P,T-space. It is further to be expected that phase transition kinetics will be studied with time resolutions heretofore unfathomable. For example, existing multichannel analyzers can be operated in the multichannel scaling mode and thus used to monitor an EDXD peak intensities in msec time intervals. By using more brilliant SR sources, either from higher energy electron orbits or on selected wiggler lines, μsec data may also be possible. In either case, kinetic data will be available for P,T-induced phase transitions which are completed in sub-second time periods. This will give researchers new insights as data are obtained from regions closer and closer to the actual critical point.

As electronic areal detectors become more available, it is to be expected that there will also be an increased growth in high pressure single crystal measurements; this, in turn, will permit detailed studies of somewhat more complex crystalline systems. It is entirely reasonable to expect the number of high pressure users and the sophistication of their experiments to grow as the availability of SR-ports grows. Perhaps future experiments will involve the production of *in situ* x-ray movies of structural phase transitions.

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Dr. Earl F. Skelton is Head of the Phase Transformation Section in the Condensed Matter and Radiation Sciences Division of the Naval Research Laboratory and a Professorial Lecturer in the School of Engineering at George Washington University. He has been engaged in high pressure research for more than 15 years. Recently, he completed an in depth review of the status of high pressure science and technology in Japan and spent a sabbatical year at Stanford University where he developed the facility for ultra-rapid structural studies under conditions of elevated pressure described in this article at the Stanford Synchrotron Radiation Laboratory.

Research Notes

Making Food from Sawdust

Making food from sawdust has recently become a real possibility because of shipworm research sponsored by the Office of Naval Research (ONR).

While studying the shipworm—a destructive, wood-eating, bivalve mollusk—researchers John B. Waterbury of Woods Hole Oceanographic Institution and C. Bradford Calloway and Ruth D. Turner of Harvard discovered a unique, new bacterium which appears capable of making protein from wood.

The new species of bacterium (as yet unnamed) is found in mass in the shipworm's gland of Deshayes, located between the gills and esophagus. What makes the bacteria unique is the fact that it can digest cellulose (in this case wood) *and* fix nitrogen, which is essential to proteins but lacking in wood.

The discovery of the presence of the bacterium explains how shipworms live off of wood without an enzyme to breakdown the cellulose material, and how they can make proteins without a source of nitrogen. It appears to work like this: the bacteria produce an enzyme (cellulase) which breaks the wood (cellulose) down into sugars—providing nourishment for the shipworm and the bacteria; the bacteria then take nitrogen gas, dissolved in the water that flows through the gills, and combines it with the sugar—making proteins.

Nitrogen-fixing bacteria are common on the roots of soybeans, peas, and other legumes; and many invertebrates host cellulose-digesting bacteria, but to date even genetic engineers could not create a single bacterium capable of both.

The new bacteria are of commercial interest because they may be able to convert wood and wood products into useful proteins, suitable for fertilizers and animal feed.

(Eric Hartwig, ONR)

New Lower Cost Permanent Magnets

During the past year, a powerful new permanent magnet material has been developed. This new magnet is based on an intermetallic compound $Fe_{14}(Nd,Pr)_2B$, discovered by a research group at the Kollmorgen Corp. which was sponsored by the Office of Naval Research as well as by independent efforts at the General Motors Research Laboratories and in Japan at Sumitomo Special Metals Corporation.

This new material is exciting in two respects. First, it has been demonstrated that one can produce a magnet having an energy product at least one third higher than the highest previously achieved. The energy product is the most commonly used figure of merit for permanent magnets; it depends on both the strength of the magnetic field produced by the magnet and the magnet's resistance to demagnetization by opposing magnetic fields. Secondly, the new magnets are expected to be of relatively low cost. Previously available magnets having high energy products are based on cobalt-samarium compounds (e.g. Co_5Sm) and are quite expensive (e.g. $100 per pound). Cobalt is considered to be one of the most important "critical materials" and at about $12 a pound is relatively expensive; almost all of the cobalt used in the U.S. is imported. Cobalt suffered from severe supply disruptions and large price increases several years ago. Further, the inclusion of cobalt in magnets reduces the amount available for other uses such as the major use of cobalt which is as a component of superalloys, essential for building advanced gas turbine engines. Further, samarium is one of the less abundant rare earth elements and is expensive.

In contrast, the new magnets consist primarily of readily available iron. The new magnets contain about 30 weight percent of neodymium and/or praseodymium, two rare earth elements which are significantly more abundant than samarium and of lower price. Further, while the total availability of Co and Sm provide limits as to the total amount of cobalt-samarium magnets that can be produced, these new magnets should be available in greater volume. The price of this new magnet material can thus be significantly lower both because of lower raw materials cost and the efficiencies possible for larger scale production.

These new magnets are attractive for a wide range of applications, both for defense and the commercial market. The application potentially requiring the largest volume of such magnets is in electric motors having increased energy efficiency and only half the size and weight of conventional motors. Other applications center on electronic devices, ranging from loudspeakers to microwave tubes to the new nuclear magnetic resonance medical imaging systems.

Given the advantages of these new magnets, companies are now working towards their commercial production. As for the Co-Sm based magnets, it is expected that a range of magnets having somewhat different properties and prices, suited to different applications, will become available. Ongoing research is directed at lowering the rate at which the energy product decreases as the temperature increases, an important characteristic for applications where the magnet must operate somewhat above room temperature.

(Donald E. Polk, ONR)

Longer-Life Aircraft Bearings

Scientists at the Naval Research Laboratory have demonstrated that chromium ion implantation can prevent corrosion in steel bearings used in Navy aircraft. The application of this new technique could save the Navy millions of dollars in maintenance costs

To field test the new process, NRL chromium-implanted bearings were installed in 10 Navy F–4 fighter planes and 13 Navy H–46 helicopters at the North Island Naval Air Station, San Diego, California. After more than a year of flight tests, none of the treated bearings, used in the F–4's turbojet main-shafts and in the rotor systems of the helicopters, has been replaced. However, in one instance, a similar untreated bearing in one of the test aircraft has failed.

Ion implantation is a process in which virtually any element can be injected into the near surface region of a solid by a directed beam of high-energy ions. During this process, energies from tens to hundreds of kilovolts are used to produce alloy concentrations of up to 30 atomic percent of the implanted element to depths of four microinches.

The advantage of ion implantation is that it produces a highly corrosion-resistant surface alloy while retaining the mechanical qualities and strength of the original alloy steel bearing. In the present case, AISI M50 steel bearings were treated to produce corrosion-resistant stainless steel surfaces by implanting their surfaces with chromium. (Due to the low strength of stainless steel, it cannot be used to fabricate an entire bearing.)

The corrosion of the bearings in aircraft turbojet engines, especially at sea, has been a particular concern for the Navy. Chlorine in the air of the marine environment accelerates pitting corrosion at the contact points between the bearings and their races, especially during periods when the engines are shutdown between flights. Bearings can also corrode while stored on the shelf. Once corrosion pits are formed they become starting points for fatigue cracks which can lead to bearing failure.

This problem can be corrected by ion implantation at a treatment cost of about 10 percent of the cost of the bearing. Accordingly, significant savings can be achieved for mainshaft bearings which cost as much as $2,500.

NRL chromium-implanted bearings have completed service tests, performed in conjunction with the Naval Air Propulsion Center, to qualify them for flight testing. The bearings are now in the in-service test stage.

In a related NRL program, studies are being conducted to develop optimum ion implantation processing methods and to perform an ecnomic case study on ion implantation. A prototype facility using the NRL-developed technique is being designed by Spire Corporation in Boston, Massachusetts, and will be operational in about a year.

NRL's research on corrosion protection began 6 years ago with studies on the measurement of the corrosion resistance of surfaces. Ion implantation has many other potential applications where surface treatment can modify a material's properties. This technique is now under development at NRL for such diverse applications as wear protection, optical filters and high-conductivity polymers.

(Graham Hubler, NRL)

Navy and Marine Corps Recognize Science, Engineering Students

The Navy does more than encourage students to pursue scientific and engineering careers; it provides fiscal support to promising high school students and post-graduate-level students.

High School Students

At the high school level, the Navy Science Awards Program, administered by the Office of Naval Research (ONR), provides recognition to outstanding students who participate in more than 300 state and regional science and engineering fairs. The Navy invites principal winners at these fairs to compete in the Navy National Science Awards competition from which 20 awardees win a two week scientific-oriented trip to Hawaii, including visits to Navy and Marine Corps activities. The top four winners also receive scholarships of $5,000, $3,000, $2,000, and $1,000.

At another annual high school student competition — the International Science and Engineering Fair — the Navy and Marine Corps participate by awarding four $10,000 scholarships and five sponsored trips to the London International Youth Science Fortnight.

In these competitions, the students' abilities and science projects are judged by scientists and engineers from the Naval Reserve Corps and the staff of ONR. The scholarship money is put aside for students until they enter college.

The winners for 1984 are listed below by name, town, and description of winning project.

Navy National Science Award Winners

First place, $5,000 scholarship, to Arthur J. Kudla of Warren, Michigan, who developed a rapid method to detect and predict the ability of different chemical compounds to cause toxic effects to adult and developing organisms.

Second place, $3,000 scholarship, to Alan J. Hu of La Jolla, California, who used calculus, algebra and numerical methods to determine the most efficient way to search very large sorted tables.

Third place, $2,000 scholarship, to Kirsten E. Luther of Basking Ridge, New Jersey, who studied chemical bonding in vanadium compounds.

Fourth place, $1,000 scholarship, to Gregg A. Feinerman of Miami Beach, Florida, who proposed a theraphy for advanced cancer patients which might prevent the spread of the disease to normal cells.

Jeffrey R. Ambroziak, Springfield, Virginia, who developed a model for predicting drought conditions in Puerto Rico. Robert M. Beglin of Beverly Shores, Indiana, fused electrically normal and cancerous lung cells as a tool for identifying cancer cell lines; William J. Bencze of Saratoga, California, developed a computer system with parallel processing ability that can execute multiple interacting programs at the same time; Sandy Chang of Bronx, New York, constructed a reflecting telescope and associated drive apparatus with which to

observe a class of variable stars, and Katherine E. Eda of Secaucus, New Jersey, applied mathematical progression known as the Fibonacci series to biological phenomena.

Rachelle F. Folse of Napoleanville, Louisiana, generated solutions to Linear Diophantine Equations and applied them to cryptography; Melaine E. Gann of Thibodaux, Louisana, studied the effects of various concentrations of outboard motor exhaust on the survival of green algae in natural waters; and Kimberly A. Karrick of League City, Texas, standardized a life support system for organisms while in orbit on a space shuttle mission.

James D. Kerner of Elkins Park, Pennsylvania, identified the chromosomal location of the New Zealand black mouse, encoding for production of antibodies; Nancy A. Kozanecki of Niles, Illinois, discovered many fascinating mathematical properties of "Magic Squares" and devised general rules for several of their properties; and Bruce E. Loebrich of Maumee, Ohio, displayed in three dimensions projections of hyperfigures of more dimensions, which can be drawn with perspective to assist students in grasping concepts of n-dimensional figures.

Mark D. Owens of New Buffalo, Michigan, developed a method using halograms to measure very small deflections of glass fiber reinforced plastics under small binding forces; Silvia M. Pulido of Titusville, Florida, studied human lung cancer and showed that chromosomes in blood cells from cancerous patients had weak links in the chromosomal chain; and Kenneth B. Walker, Charlotte, Tennessee, developed a practical and economical method for removing metal pollutants from industrial waste water.

Steven F. Wolfe, Bayside, New York, studied the use of electrochemical methods for the reduction of organic oxygen compounds; and David M. Zielke of Merritt Island, Florida, developed a computer control system to monitor large industrial research laser systems.

Navy/Marine Corps International Science and Engineering Fair Winners

The four $10,000 scholarship winners are: Angela Philpot of Rockledge, Florida, who studied the effects of pentylentetrazol on the catecholamine level in the gold fish (*Carassius Auratus*) brain; Arthur J. Kudla of Warren Michigan, who also won the first place Navy National Science Award (see above); William J. Bencze of Saratoga, California, who developed a computer system with processing ability that can execute multiple interacting programs at the same time; and Martin Shipley of Los Alamos, New Mexico, who fabricated a computer-controlled spectrophotometer and a stopped flow/continuous flow reactor to monitor changes in chemical components and their rates of reaction.

Students who won trips to London are Lisa Knight of Grand Bay, Alabama, who studied bacteria infecting the lungs of patients with cystic fibrosis and found that the lungs surround themselves with alginate, a thick material which frustrates the body's defense mechanism against bacteria; Kevin L. Linduaer of Denver, Colorado, who studied the environmental factors that contributed to germination of mountain mahogany in Colorado; Nathan A. Shapira of Atlanta, Georgia, who discovered a protein bound to mitochondrial DNA, and examined its role in aging and cancer; Jeffrey R. Ambroziak of Springfield of Virginia, who also won a Navy National Science Award (see above); Craig K. Rogers of Winchester, Virginia, who studied the effect of airfoil design, blade pitch, center of pressure, and rotational speed on helicopter noise levels and comparative lift-efficiency.

Graduate Fellows

As a means of increasing the supply of U.S. civilians trained in areas of science and engineering critical to the Navy, ONR sponsors a graduate fellowship program. This year, 34 outstanding graduate students were awarded fellowships to support their research and studies leading to doctoral degrees. The ONR Graduate Fellows will receive stipends of $13,000 for the first year, $14,000 for the second year, and $15,000 for the third year. In addition, ONR will pay the Fellow's full tuition and $2,000 per year to the Fellow's department. From previous years, there are 113 Fellows participating in the program.

The Fellows selected for 1984 are listed below by name, university, and scientific field of interest:

Anthony, LaVigna, University of Maryland, signal processing; Ronald Emmanuel Pekar, California Institute of Technology, solid state/integrated circuit; Kevin Lee Lear, Boulder, Colorado, solid state devices; David C. MacEnay, University of Maryland, signal processing; Timothy Griesser, Arizona State University, electro-magnetics; Jonathan B. Amsterdam, Harvard University, artificial intelligence; Claire Margaret Bono, University of California at Berkely, artificial intelligence; Christopher Truxaw, Calofornia State University, artificial intelligence; Philip Nathan Klein, Harvard University, algorithms; Andrew T. Phillips, Pennsylvania State University, artificial intelligence/ robotics; Chris Gronet, (former Navy National Science Award Winner) Stanford University, optical electrical materials.

Frederick James Von Priessig, Stanford University, magnetic materials; Steven Paul Den Baars, University of Arizona, optical, electrical, and magnetic materials; Kathryn Lynn Fink, Michigan Technical University, reliability and non-destructive evaluation; Stanislaus A. Zygmunt, Massachusetts Institute of Technology, optical, electrical, and magnetic materials; Peter V. Minnick, University of Colorado, ship hydrodynamics; Keith Michael Garman, Vanderbilt University, geological oceanography and remote sensing; Walter Dean Mieher, University of Illinois, surface physics; Stephanie Anne Gajar, The Pennsylvania State University, electronics.

Michael S. Engber, University of Missouri, applied physics; David J. Brady, Macalester College, opto-electronics; Henry Edward Fischer, Yale University, laser physics; Guy D. Gilliland, Baylor University, laser physics; David J. Patterson, Rose-Hulman College, propulsion; Norman Gene Gwinn, Texas A&M University, computational fluid dynamics; Mark J. Lewis, Massachusetts Institute of Technology, propulsion.

Kyle David Squires, Washington State University, computational/ experimental fluid dynamics; Cheryl Ann Harper, University of Delaware, computational methods; Gary Lee Brem, The Pennsylvania State University, genetic engineering and bio-polymers; David Robert Breitbach, Iowa State University, neuroplasticity; Hugh Charles Crenshaw, Australian Institute of Marine Science, neuroplasticity; Thomas M. Bugbee, U.S. Congress OTA, microbial genetics; Annette Suzanne Parent, University of Santa Clara, genetic engineering; and Keith Albert Matthews, Jackson State University, molecular biology.

(Barbara Thurman, ONR)

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